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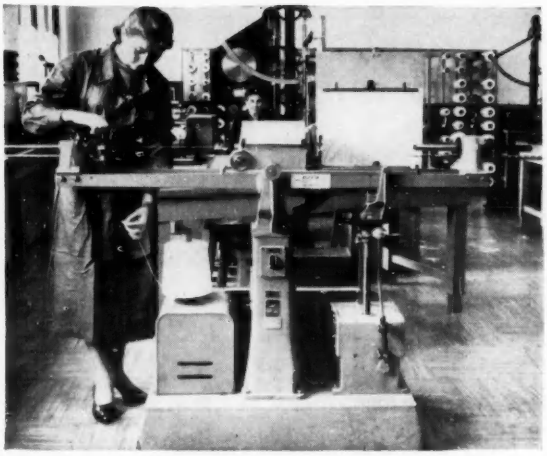

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# The Colour Index

THE second edition of THE COLOUR INDEX is nearing completion and will be published in four volumes, the first of which will be ready for delivery before the end of this year. Volume II will follow soon thereafter. Volumes III and IV are scheduled to appear early in 1957. Preparation and publication of this work is the joint effort of The Society of Dyers and Colourists (Great Britain) and The American Association of Textile Chemists and Colorists.

This edition has been completely redesigned and brought up-to-date with the cooperation of all the dye manufacturers in Great Britain, America, Western Europe, and Japan. The cost, at time of going to press with this announcement, had not been established but will be in the vicinity of $100.00. Subscriptions to the Index may be sent to The American Association of Textile Chemists and Colorists or to The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire, England.

TEXTILE RESEARCH JOURNAL

VOL. XXVI, NO. 10 OCTOBER 1956

# The Effect of Yarn Twist on Fabric Crease Recovery

**Richard Steele**

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**Abstract**

When fabrics are bent or creased in other than the warp or fill directions, the deformation of the individual yarns has a torsional component. The interaction of this component with the twist of the yarn should result in anisotropic creasing behavior in the fabric.

Crease recovery as a function of test direction was measured for a number of fabrics. Anisotropy attributable to torsion-twist interaction was found in cellulosic fabrics when strong directional effects due to such factors as twill ribs were not introduced by the fabric construction. The effect could be qualitatively related to the yarn twists. With fibers of greater intrinsic resilience, such as wool, nylon, or acetate, the crease recovery was essentially isotropic.

When cellulosic fabrics were treated with dimethylol urea, their crease recovery not only became greater but also was more nearly isotropic.

THE ability of a fabric to recover from a creasing deformation depends to a large extent upon the mechanical properties of its component fibers, but it is also influenced to some degree by the construction and geometry of the fabric. The effects of the latter have attracted relatively little attention, and not much information is available in this field. Hamburger and others [2], working with a series of acetate fabrics, explored some relationships between weave and crease recovery. They found that texture had an effect which was more pronounced in staple yarn fabrics than in filament yarn fabrics, and that yarn twist had a small effect. The effect of twist has been studied in more detail by Ikeda and Okajima [3], who observed that the crease recovery of cotton fabrics in general decreases with increasing yarn twist, although sometimes it increases or goes through a maximum or minimum. These results were interpreted in terms of the relative intensities of two factors, the freedom of motion of individual fibers in the yarn, which decreases with twist, and the reinforcement of the yarn structure due to the increasing twist.

Jameson, Whittier, and Schiefer [4] studied a series of viscose-rayon-filament fabrics in which the filling denier and picks per inch were systematically varied and found that changes in these parameters did not affect crease recovery. Similarly, Krasny, Mallory, Phillips, and Sookne [5] found little effect on crease recovery when yarn properties were varied only in the filling direction, but observed that crease recovery is generally improved by open construction,

that is, for a given fabric weight, by using high yarn denier and wide yarn spacing. Their work was done on a group of fabrics made from Fortisan.

This laboratory has recently been studying the torsional properties of fibers and yarns and the importance they have in certain aspects of fabric behavior. In the course of this work, it was suggested that when a fabric was creased along a line not parallel to either set of yarns, the crease recovery might be affected by the twist of the component yarns to a degree dependent upon the angle between the crease line and the yarn direction. Such anisotropy in creasing behavior would probably affect drape and other factors in the hand of the fabric. Investigation has shown that anisotropy of this sort exists in the crease recovery of some cotton and rayon fabrics, but it has not been observed in fabrics made from fibers having high intrinsic resilience.

How this twist effect should be expected to arise can be shown with the help of Figure 1, which shows a small strip of fabric cut so that its warp yarns make an acute angle with the long direction of the sample. When the sample is folded and creased so that its ends *a* and *b* are together, warp yarn *cd* is deformed into *c'd*. This deformation is equivalent to bending the yarn back on itself, as in a warp-direction test, and twisting it through the angle $\tau$. If this folding twist angle is in the direction of the yarn twist, the resistance of the fabric to bending will be enhanced; if the fold twist angle is in the opposite direction from that of the yarn twist, the resulting untwisting of the yarn will add to the stability of the folded formation and should result in reduced crease recovery.

If yarn *cd* in Figure 1 is considered when the fabric is folded up out of the plane of the paper, its folding twist angle will be in the "S" direction as the test angle $\alpha$ increases from 0° to 90°. From 90° to 180° the folding twist angle is in the "Z" direction. If the fabric fold is made in the opposite direction, that is, ends *a* and *b* are brought together below the paper, the resulting folding twist angle is reversed in direction. Similar relationships are obtained for the filling yarns. All these relationships are summarized in Table I.

The first and third quadrants are the same, as are the second and fourth, so that the test angle may be measured clockwise from the warp direction without regard to endwise orientation. On fabrics without apparent face, like sheeting, turning the fabric over will make no difference if the conventions for making the fold and measuring the test angle are observed.

**TABLE I. Yarn Twisting Effect of Fabric Folding**

| | Direction of twist resulting from face-to-face fold | | Direction of twist resulting from back-to-back fold | |
|---|---|---|---|---|
| Test angle* | Fill | Warp | Fill | Warp |
| 0° to 90° | Z | S | S | Z |
| 90° to 180° | S | Z | Z | S |
| 180° to 270° | Z | S | S | Z |
| 270° to 360° | S | Z | Z | S |

* Measured clockwise from warp direction.

There are a number of important effects involved in the physical picture of creasing fabric on the bias. Some of these are perhaps capable of being separated and treated more analytically than has been possible in the present work. For example, it might be possible to treat in greater detail the changing directions of restoring bending and torsional movements in the yarn, the nonlinear bending and torsional characteristics of the yarns, the changing curvature of bending in warp and filling yarns, as well as other factors.

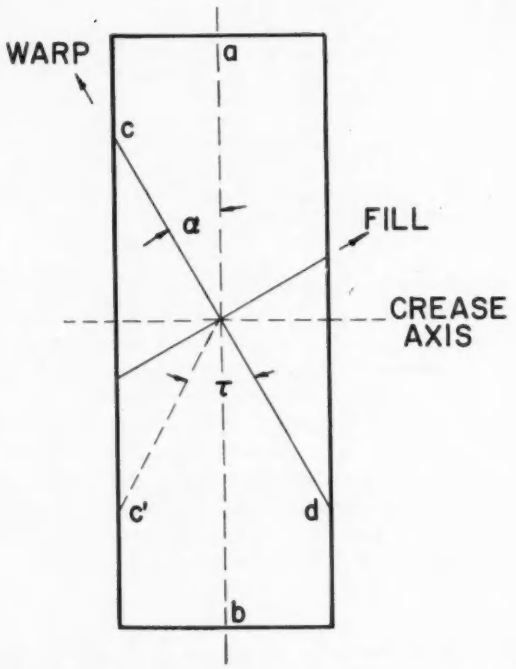


**Fig. 1.** Relationship of folding twist effect $\tau$ to test angle $\alpha$ in crease recovery.

## Experimental Part

The fabrics which have been tested are described in Table II. Crush-resistant samples of the cotton print cloth and rayon challis were prepared by treatment with a 12% solution of dimethylol urea, using 0.1% ammonium chloride as a catalyst. The samples were dried on frames and cured at 150° C. for 10 min.

Although a more direct measure of creasing resistance would perhaps have been desirable, the degree of crease recovery was used to evaluate the creasing properties of the fabrics. It was determined by a modification of the Tootal-Broadhurst-Lee method. A 1 × 4-cm. sample was folded, placed under a thin leaf spring, and weighted with a 500-g. weight. After 5 min. the sample was removed and allowed to relax for 3 min. while hanging over a taut wire. The per cent angular recovery was then measured in a protractor device similar to the Monsanto instrument [1], where the free end of the sample hangs vertically when the measurement is made.

A circle approximately 16 in. in diameter was laid out on the fabric. Diameters were drawn in the warp and fill directions and at the desired intermediate angles, usually at 10° or 15° intervals. With a rubber stamp, four 1 × 4-cm. test strips were marked off on each end of each diameter. For 10° intervals this made a total of 144 test strips. Two in each group of four were tested with a face-to-face fold; the others were folded back-to-back. Data from angles of 0° to 90° were equivalent to those from 180° to 270°, and similarly for the second and fourth quadrants. Thus each value was replicated four times. The results are most easily visualized by using a plot of average crease recovery against test angle on polar coordinate paper, as shown in Figure 2. These plots are referred to as crease recovery patterns. When the figure caption indicates that the face-to-face data have been "reflected," this means that the mirror image of the face-to-face pattern has been plotted.

## Results and Discussion

The anisotropy of the crease recovery is very apparent in the results obtained with print cloth, broadcloth and challis, as shown in Figure 2. As expected, the data from face-to-face folding are the mirror image of back-to-back folding.

The cotton print cloth was probably designed to be a balanced fabric, the difference in warp and fill yarns probably having arisen from warpwise stretch during desizing and bleaching. With equal twist in warp and fill yarns, it might be expected that the effect of torsion on the isotropy of crease recovery might not be apparent. For instance, in quadrant I of the pattern for print cloth in Figure 2, the positive twist effect in the warp yarn increases as $\alpha$ is increased from 0° to 90°. The negative effect in the filling yarns decreases at the same time. If the yarns are identical and the effects balance one another, then no anisotropy due to torsion effects should be apparent. The pronounced anisotropy in the crease re-

**TABLE II. Experimental Materials**

| Fabric | Warp | | | | Fill | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Yarn count* | Twist | | Ends/ inch | Yarn count* | Twist | | Picks/ inch | Weight oz./sq. yd. |
| | | TPI | Direct. | | | TPI | Direct. | | |
| Cotton print cloth | 35's | 21 | Z | 84 | 40's | 23 | Z | 78 | 3.1 |
| Cotton broadcloth | 36's | 24 | Z | 120 | 53's | 22 | Z | 60 | 3.3 |
| Cotton twill | 20's | 19 | Z | 110 | 26/2 | 25‡ | Z | 58 | 6.0 |
| | | | | | | 16† | S | | |
| Rayon challis | 28's | 17 | Z | 84 | 33's | 18 | Z | 64 | 3.4 |
| Acetate satin | 70 | 3 | S | 86 | 144 | 3 | S | 62 | 3.0 |
| 60/40 Rayon-wool gabardine | 25/2 | 17‡ | Z | 62 | 20's | 12 | Z | 53 | 9.3 |
| | | 18† | S | | | | | | |
| Plain weave, spun nylon | 39/2 | 84‡ | Z | 59 | 34/2 | 90‡ | Z | 51 | 2.2 |
| | | 21† | S | | | 21† | S | | |
| Plain weave, filament nylon | 78 | 8 | Z | 112 | 160 | 7 | Z | 85 | 3.0 |

* Cotton count is given except for the filament acetate and nylon, which are in denier, and the rayon-wool blend, which is worsted count.

† Singles.

‡ Ply.

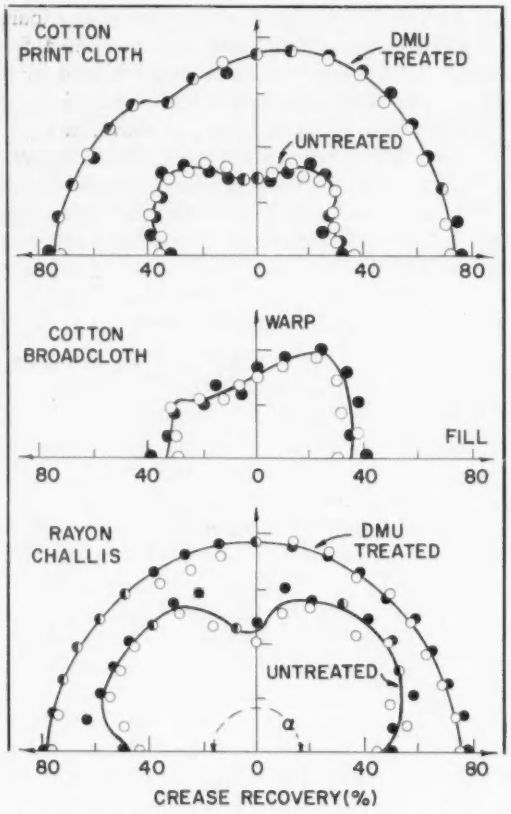


**Fig. 2.** Crease recovery patterns for cellulosic fabrics plotted in polar coordinates where $\alpha$ is the test angle. Open circles are points for back-to-back fold; solid circles are reflected points for face-to-face fold.

covery of the untreated print cloth shows this simple picture is not true.

The twist effect attributable to a given set of yarns is, of course, zero in the direction of those yarns. The picture above indicates that the maximum effect would be at $\alpha = 90°$, that is, in the direction of the other set of yarns. However, at 90° the effect is actually zero since there is no effective torque applied to the yarn when it is in the axis of the fold. If one assumes the longitudinal yarn is folded at the crease over a rod equal in diameter to the transverse yarns, the expression for the geometric torsion of the bent yarn should be $(\sin 2\alpha)/2r$, where $\alpha$ is the test angle and $r$ is the radius of the rod. This expression is zero for $\alpha$ equal to 0° or 90° and has a maximum for $\alpha = 45°$. There can be a maximum in the effect of twist on crease recovery at an intermediate angle, as shown in Figure 2, but the measured maximum does not occur at 45° for print cloth or broadcloth. These results suggest that the maximum is shifted to an angle less than 45° by factors not considered here. In this case the shape of the pattern for untreated print cloth could perhaps be qualitatively explained by assuming that the positive effect of the warp yarns predominates in the half of quadrant I nearer the warp direction, while the negative effect of the fill yarns predominates in the half nearer the fill direction. This is for Z-twist yarns in samples folded face-to-face. This qualitatively describes the shape of the experimental curve for cotton print cloth. In the first quadrant there is a maximum in the crease recovery at a test angle nearer the warp direction; in the second quadrant, where the twist effects are reversed, the maximum is nearer the filling direction. In both cases the maximum is displaced in the direction of the yarns having a positive folding twist effect.

This general description above also fits the results with the broadcloth where the two sets of yarns, though differing in size, have about the same twist. However, from considerations of twist alone, it would be expected that the pattern of quadrant I would be superimposable on that of quadrant II when rotated 90° about its origin. The fact that the patterns for the untreated fabric are not superimposable after rotation is probably due to the different number of spring elements involved in the folding twist effect. The number of working yarns in a crease 1 in. wide can be expressed as sin $\alpha$ (warp ends/inch) plus cos $\alpha$ (filling picks/inch). When the thread counts of the warp and filling are the same, this function is symmetrical in each quadrant. For the broadcloth, the high warp thread count makes the positive effect stronger in the first quadrant than the negative effect of the fill. In the second quadrant the negative effect is greater. This results in a nonsymmetrical pattern for each quadrant, so that rotation through 90° does not superimpose quadrants I and II.

The crease recovery pattern of the untreated rayon challis fits the above considerations less well. Its most marked characteristics are the low recoveries measured in the yarn directions. However, the crease recovery at intermediate angles does seem to show some displacement in the expected directions. (The reviewer of this paper has suggested that these results may be explained in terms of the buckling of the yarns at the bend. For a slippery yarn, the bias

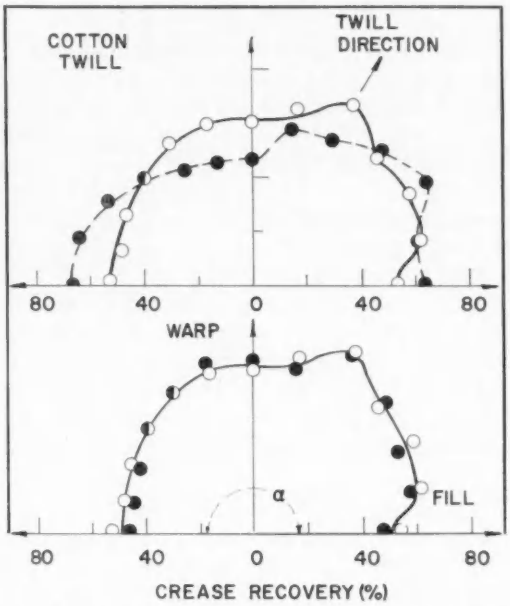


**Fig. 3.** Crease recovery pattern for cotton twill in polar coordinates where α is the test angle. Open circles are points for back-to-back fold; solid circles, for face-to-face. In the lower pattern the face-to-face points have been reflected and rotated 90°.

fold should allow for a reduction in elastic strain energy through buckling. This is less likely to occur in orthogonal folds.)

Gross directional geometrical features in a fabric would be expected to affect the crease recovery pattern. In the case of a twill or rib, the effect may be considerable, as shown in Figure 3. Here the back-to-back and face-to-face patterns do not have the same relationship as for plain weave fabrics. They are still superimposable if one pattern is rotated through 90° and then reflected. The result of this operation is shown in the lower half of Figure 3. The two "horns" of this pattern are very probably due to the twill of the fabric. The direction of the warp flush twill, which coincides with the filling flush twill on the fabric back, is indicated in the figure. Away from these peaks the points fall quite well on a regular ellipse. It has not been possible to relate the parameters of this ellipse (especially the axis ratio), or the operations necessary for superposition, to the geometry of the fabric.

The anisotropic crease recovery patterns discussed above were obtained with cellulosic fibers whose intrinsic resilience is not very great. The folding twist effect is small, and is probably most apparent on fabrics where the fibers themselves have little ability to recover from bending to the angles involved in creasing. Fabrics made of fibers having high intrinsic recovery may always be so good in crease recovery that folding-twist or geometrical effects may be masked, and, in fact, anisotropy attributable to the effect of yarn twist has not been observed in such fabrics. Their high intrinsic crease recovery apparently does mask any effect. Some results on more resilient fabrics are shown in Figures 4 and 5. These patterns are for acetate, viscose-wool, and nylon fabrics, whose average crease recovery is 70 to 80%. The average crease recovery for the cotton broadcloth and print cloth, which show the effects of twist most markedly, is 35%. The spun-rayon challis and the cotton twill, which show smaller effects, have average crease recoveries of 60% and 56%, respectively. The effect of twist on crease recovery observed by Ikeda and Okajima [3] was very pronounced compared with the results of other workers [2, 5], and this may well have been due to the fact that Ikeda and Okajima worked with cotton fabrics, while the other observations were on acetate and Fortisan fabrics.

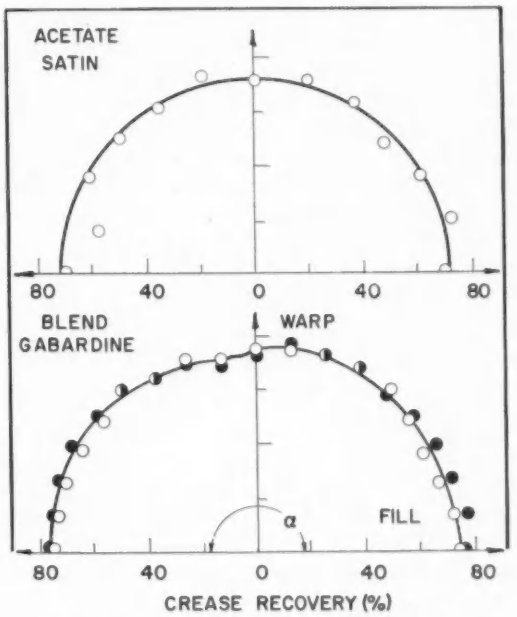


**Fig. 4.** Crease recovery patterns for acetate satin and viscose-wool-blend gabardine. Open circles are for back-to-back fold; solid circles for face-to-face.

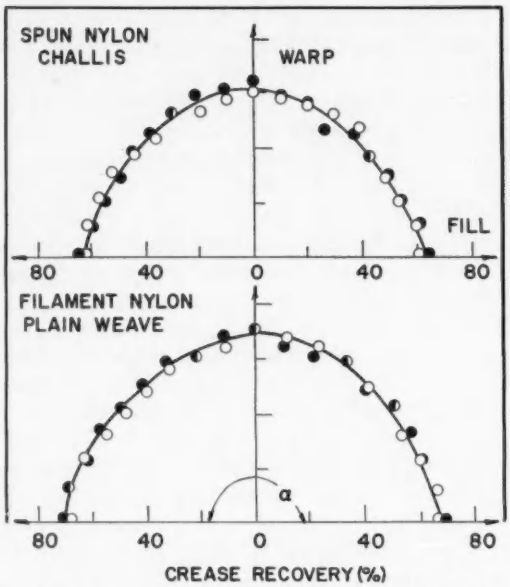


**Fig. 5.** Crease recovery patterns for nylon fabrics. Open circles for back-to-back fold; solid circles for face-to-face.

Treatment of cotton print cloth or rayon challis with dimethylol urea produces a much more isotropic crease recovery pattern. Such treatment reduces or eliminates the twist effect by stabilizing the yarn twist, and since the fiber resilience is increased, there may also be masking as observed with naturally resilient fibers. The patterns of treated cotton and rayon fabrics are shown in Figure 2. A properly chosen treatment of this sort might reduce the tendency of some fabrics to curl, which has been related to yarn twist by Whitman [6].

## Summary and Conclusions

From consideration of the deformation of yarns in fabric samples folded at an angle to both warp and filling threads, it was predicted that yarn twist would produce anisotropic creasing properties in many fabrics. Such anisotropy has been observed in the crease recovery of fabrics whose fibers have low intrinsic resilience and whose structure is not complicated by gross directional geometrical factors.

The best examples found were fabrics made from cellulosic fibers. Resin treatment similar to that ordinarily applied for crushproofing such fabrics produced more nearly isotropic crease recovery patterns. Fabrics made of fibers with high intrinsic resilience, such as nylon, acetate, or wool, do not show any crease recovery effect attributable to yarn twist.

## Acknowledgment

The experimental work reported in this paper was carried out by Mrs. Angela Simonson.

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*Manuscript received January 12, 1956.*

# The Reaction of Formaldehyde with Cellulosic Fibers

## Part I: Rate and Mechanism of the Reaction[1]

**H. K. Woo,[2] J. H. Dusenbury,[3] and J. H. Dillon[4]**

*Textile Research Institute and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey*

**Abstract**

The acid-catalyzed reaction of formaldehyde with cellulose has been studied under conditions comparable to those of formaldehyde treatments carried out in textile finishing plants. Cotton, Fortisan, and viscose rayon fabrics were treated at different pad-bath pH values (2.0, 2.2, and 2.4) and formaldehyde concentrations, at different temperatures (110°, 120°, and 130° C.), and for different periods of time.

At the higher pH values of 2.2 and 2.4, the cross-linking reaction seems to take place primarily in the amorphous regions of the fibers; at the lowest pH, a very rapid reaction occurs in the amorphous regions, accompanied and followed by diffusion of formaldehyde into the crystalline regions which controls the observed reaction rate. Both the rate and extent of reaction appear to depend on the state of internal order of the cellulosic material, being least for cotton, the material of highest crystallinity. Fortisan and viscose rayon have about the same degree of crystallinity, but the reaction with Fortisan is more rapid which causes the extent of reaction at later times to be greater than that observed for viscose rayon. Two possible explanations are either that the higher orientation of Fortisan facilitates the cross-linking process or that recrystallization occurs during acid hydrolysis, and viscose rayon has a relatively higher rate of recrystallization. The results of X-ray diffraction studies carried out on the variously treated cellulosic fibers are consistent with the proposed reaction mechanisms.

### Introduction

Since the discovery by Eschalier in 1906 [6] that a treatment of regenerated cellulosic fibers with formaldehyde under acidic conditions improves their wet strength, the formaldehyde–cellulose reaction has been investigated extensively. Reviews of literature on the reaction can be found in several prior studies, notably those of Wood [26], Schenk [19], Dillenius [5], Schaeffer [18], Heuser [11], Gruntfest and Gagliardi [8], and Wagner and Pacsu [21]. Most of the earlier efforts were made to determine the structure of the reaction product. The consensus was that under acidic conditions the reaction leads to the formation of methylene-ether cross-links such as $Z\text{-}O\text{-}CH_2\text{-}O\text{-}Z'$, where $Z$ and $Z'$ are glucosidic residues in cellulosic chains. The $Z$'s are most likely in adjacent chains of cellulose. Cross-linking between hydroxyl groups on the same glucopyranose unit was generally believed to be unlikely on the grounds that the structure resulting from such a reaction would contain strain and be unstable. Furthermore, the formation of such a reaction product could not explain the observed changes in properties such as decreased swellability, reduced dye uptake, and altered mechanical properties. Wagner and Pacsu [21], in their study, showed that formaldehyde reacted preferentially with the secondary hydroxyl groups and that the cross-links were not polymeric. The latter conclusion has been supported by the results of infrared spectral studies made by Steele [20].

In general, the reaction conditions used in structural studies were rather drastic. Every effort was made to introduce as much bound formaldehyde as possible. Consequently, the resulting product was

[1] This paper is based upon part of a dissertation submitted by H. K. Woo in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

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[4] Director, Textile Research Institute.

highly degraded with respect to mechanical properties. In some instances, the cotton yarns that Wagner and Pacsu treated to yield products with 5.0–6.5% bound formaldehyde were too highly degraded to permit measurements of mechanical strength. From a practical viewpoint such a product is certainly not desirable, however useful it may be for carrying out structural studies. Goldthwait [7] pointed out that a bound formaldehyde content of 0.5–1.5% is enough to give cotton distinctive new properties attributable to cross-linking. He also observed that the initial state of swelling of cotton can have a decisive influence on the nature of the reaction product. Under the same treatment conditions, an air-dried cotton yarn gave a product that resisted dyeing but contained a relatively small amount of formaldehyde, while a preswollen yarn resulted in a product that contained more formaldehyde and was not as resistant to dyeing.

In the light of these findings, it appeared that a profitable venture would be to make a study of the kinetics of the reaction under conditions comparable to those employed in industrial practice, using as cellulose samples different cellulosic fibers of known variations in the state of internal order. The main objectives of this study were:

(1) To elucidate the mechanism of the formaldehyde–cellulose reaction, employing reaction conditions similar to those used in industrial practice.

(2) To make a comparative study of the rate and extent of reaction between formaldehyde and the cellulose of fibers with different states of internal order.

(3) To study the effects of the formaldehyde treatment on the mechanical behavior of the various fibers.

Work aimed at achieving the first two objectives is discussed in this paper, which is Part I of a series of two publications. The work done to achieve the third objective is covered in the Part II paper [25].

## Materials

Fabrics of three different cellulosic fibers were selected, each representing a distinct state of internal order. They were cotton, which is a native cellulose of rather high crystallinity; and viscose rayon and Fortisan, which are both regenerated celluloses of low crystallinity, with the latter having an orientation considerably higher than the former. Cloth analyses of the fabrics studied are shown in Table I.

The cotton fabric was given a mild scouring in a soap solution (2 g./liter) for ½ hr. at the boil to remove the light warp sizing and dried in a conditioned room (70° F. and 65% R.H.) before use. The Fortisan and viscose rayon fabrics (both unsized) were used as received after conditioning.

The formaldehyde solution used throughout this work was Merck "Reagent-Grade." The exact formaldehyde content was determined for each lot used by dimedone precipitation [23]. In preparing the treating baths of different formaldehyde concentrations at different pH values, the requisite amounts of formaldehyde were added to distilled water to make up the volume called for in the "Clark and Lubs" buffer mixtures used to obtain the specific pH's. These buffer mixtures have been described in detail by Clark [3].

## Experimental Procedures

In industrial practice, a formaldehyde treatment is generally carried out on the material in fabric form. Accordingly, a procedure was adopted which consisted of wetting, padding, and baking the different cellulosic fabrics. The wetting procedure consisted of immersion of a 10-in. by 15-in. fabric sample in 200 ml. of treating bath for 5 min. After this, the fabric sample was run through a padder with the pressure on the rolls set to give a 100% pickup. The pickup values were reproducible to ± 1%. The fabric was then immediately mounted on a wooden tenter frame and baked in a specially designed oven for a definite period. The pins of the frames used for this purpose were arranged along the edges of a rectangular area 8 in. by 12 in. The samples of fabric taken for subsequent formaldehyde analysis or for

**TABLE I. Cloth Analyses of Fabrics**

| Material | Cotton | Fortisan | Rayon |
|---|---|---|---|
| Yarn type | Spun staple | Continuous filament | Continuous filament |
| Weave | Plain | Plain | 2/1 twill |
| Thread count | 116 × 106 | 100 × 84 | 112 × 70 |
| Warp yarn | 54's (98.4 den.) | 50 den. | 150 den. |
| Filling yarn | 48's (110.7 den.) | 60 den. | 150 den. |
| Fabric weight (oz./yd.²) | 2.90 | 1.29 | 3.60 |
| Warp thread count × den. | 11,410 | 5,000 | 16,800 |
| Filling thread count × den. | 11,730 | 5,040 | 10,500 |

physical testing [25] were removed from the central 8-in. by 12-in. portion of the fabric sample maintained at constant dimensions during the baking operation. To offset the drop in the oven temperature following the opening of the oven door for insertion of a fabric sample, the baking oven was set initially at a temperature 10° C. above that used for baking. It was observed that 1 to 3 min. were required for the oven temperature to return to the desired baking temperature following the insertion of a fabric sample. The baking time was considered to start at the instant the desired baking temperature was attained.

The oven was constructed from ¼-in.-thick "Transite" boards. A schematic diagram showing a top and a front view is given in Figure 1. The essential features of the oven are listed as follows:

(1) It is bordered on three sides by an air duct in which are located a centrifugal blower, a bimetallic-strip-type thermoregulator, and three 600-watt "hairpin" electric heaters. In terms of the air flow through the oven, the blower and thermoregulator are placed at the exit and entrance, respectively, of the baking chamber.

(2) The baking chamber is insulated at the top, bottom, and back by 3-in.-thick spaces filled with fiber glass. The two side walls, where the exit and entrance for air flow are located, are perforated to permit the passage of air and formaldehyde vapor. Baffle boards are placed between these walls and the exit and entrance for the vapor from the duct to ensure even temperature in the chamber.

(3) The fabric to be baked is pinned on a wooden tenter frame as described previously, and this frame is placed on an aluminum rack inside the chamber, with the fabric lying in a horizontal plane parallel to the direction of air flow.

(4) The heaters are capable of bringing the baking chamber from room temperature to 140° C. in ½ hr. The control of temperature was observed to be within ± 1° C. throughout the baking chamber and during the baking period.

(5) A vent is provided in the duct to exhaust excess formaldehyde vapor from the oven after completing an experiment. During the baking operation, air, water, and formaldehyde vapors are circulated through the oven under constant volume conditions, i.e., in a closed system.

For carrying out the reaction, the following ranges of variables were used for each of the three fabric types:

(1) Initial concentration of formaldehyde in pad bath, based on the weight of fabric and a 100% pickup factor: 5.0, 7.5, and 10.0% for cotton; and 2.5, 5.0, and 7.5% for Fortisan and viscose rayon.
(2) pH of pad bath: 2.0, 2.2, and 2.4.
(3) Baking temperature: 110°, 120°, and 130° C.
(4) Baking time: 5, 10, 15, and 30 min.

For each fabric type, therefore, the experimental conditions were "cross-varied" to give a total of 108 experiments. These experimental conditions were selected on the basis of some exploratory experiments described in detail elsewhere [24]. The different pad-bath pH values were obtained by using the buffer mixtures described by Clark [3]:

For pH 2.0: 10.6 ml. 0.2*N* hydrochloric acid
50.0 ml. 0.2*M* potassium chloride per 200 ml. of solution
pH 2.2: 46.7 ml. 0.2*N* hydrochloric acid
50.0 ml. 0.2*M* potassium acid phthalate per 200 ml. of solution
pH 2.4: 39.6 ml. 0.2*N* hydrochloric acid
50.0 ml. 0.2*M* potassium acid phthalate per 200 ml. of solution

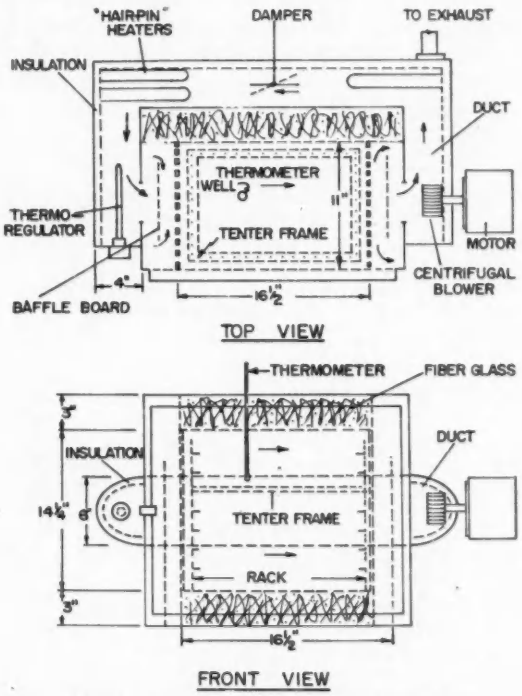



**Fig. 1.** Schematic diagram of baking oven.

After baking for a specified period, a fabric sample was removed from the oven and "boiled off" in a solution buffered at pH 7.0. This was done to remove any formaldehyde not covalently bound to cellulosic hydroxyl groups [8, 20, 21]. The changes in the properties of cellulose caused by the acid-catalyzed reaction with formaldehyde indicate that a major portion of the covalently bound formaldehyde is in the form of cross-links between cellulosic hydroxyl groups [7, 8, 20, 25]. After ½ hr. of such boiling, the fabric was washed thoroughly with hot water, mounted on the wooden tenter frame used for baking, and allowed to dry overnight in a conditioned room (70° F. and 65% R.H.). The "bound formaldehyde" in the fabric was determined by taking a 0.500-g. sample of the dried fabric, allowing it to hydrolyze overnight in 50 ml. of 12*N* sulfuric acid, and analyzing the hydrolyzate for formaldehyde with chromotropic acid by the colorimetric procedure developed by Bricker and Johnson [2].

### Results of Chemical Rate Studies

Figures 2 (cotton), 3 (Fortisan), and 4 (rayon) illustrate the relationships between the measured amounts of bound formaldehyde, $x$, and the initial concentrations of formaldehyde in the padding baths, $a$. It may be seen that the majority of the points fall well on the corresponding straight lines drawn through the origin; i.e., the amount of bound formaldehyde resulting from treatment appears to be directly proportional to the amount padded on the fabric initially. This apparent linear relationship agrees with the findings of some previous investigators [5, 8]. Each straight-line plot shown in Figures 2, 3, and 4 passes through the origin and has a slope which is the average of the three slopes that would be obtained if straight lines were drawn from the origin to each one of the three points corresponding to the three different initial concentrations of formaldehyde.[5] The slope of each straight line shown in Figures 2, 3, and 4 is equal, therefore, to a single value of the ratio $x/a$, and represents the average of three different experimental determinations of $x/a$ for a given fabric, pH, baking temperature, and baking time.

If these $x/a$ ratios, which are indices of the extent of reaction, are plotted against the baking times, reaction rate curves are obtained that are shown in Figure 5 for cotton, Fortisan, and rayon. These curves are similar in shape to rate plots for the hydrochloric-acid hydrolysis of cellulose [4, 16, 17]. It will be noted that they have a linear portion which can be extrapolated to zero time. The slopes of these straight lines represent rate constants, and the intercepts on the ordinates provide measures of a fast reaction (or reactions) that takes place very rapidly. The general equation for the straight lines is:

$$x/a = kt + C$$

where $x/a$ is the ratio of formaldehyde bound to formaldehyde applied (assuming 100% pickup), $t$ is time, $k$ is the slope and rate constant, and $C$ is the intercept and measure of an initial, very rapid reaction.

Although the straight lines in Figure 5 are shown drawn through four points in each case for convenience in representing the data, it should be borne in mind that each of the points is the average of three $x/a$ values. The values of $k$ listed in Table II and of $C$ listed in Table III were obtained by the method of least squares, and each value was derived from a total of twelve experimental determinations. The limits shown in Tables II and III are 95% confidence levels for the corresponding values of $k$ and $C$.

**TABLE II. Calculated Rate Constants**

| pH | $k$ (sec.$^{-1}$) × $10^6$ 110° C. | 120° C. | 130° C. |
|---|---|---|---|
| | Cotton | | |
| 2.0 | 2.71 ± 0.76 | 3.27 ± 0.63 | 4.12 ± 0.85 |
| 2.2 | 0.508 0.069 | 1.011 0.335 | 1.440 0.355 |
| 2.4 | 0.351 0.051 | 0.583 0.158 | 1.007 0.268 |
| | Fortisan | | |
| 2.0 | 7.23 ± 2.05 | 7.73 ± 2.19 | 9.33 ± 2.68 |
| 2.2 | 1.104 0.350 | 1.689 0.323 | 2.771 0.929 |
| 2.4 | 0.470 0.173 | 1.133 0.321 | 1.472 0.355 |
| | Rayon | | |
| 2.0 | 3.94 ± 1.73 | 4.15 ± 1.14 | 5.25 ± 1.64 |
| 2.2 | 0.716 0.132 | 1.360 0.232 | 1.814 0.258 |
| 2.4 | 0.353 0.081 | 0.781 0.131 | 1.052 0.193 |

[5] This method of averaging slopes is not strictly rigorous and is subject to criticism, since it involves the assumption that the origin of coordinates is a point of absolute accuracy. The procedure may be justified only on the basis of "chemical intuition" which infers that there can be no bound formaldehyde when there is zero initial concentration of formaldehyde in the pad-bath solution. Several comparisons of the results obtained by this method with those derived by conventional statistical approaches, in which the origin (as an experimental point) is assumed to have as much uncertainty as the other experimental points, have been made; only trivial differences were found. Hence, the average slope technique was used for simplicity, but its questionable generality is acknowledged.

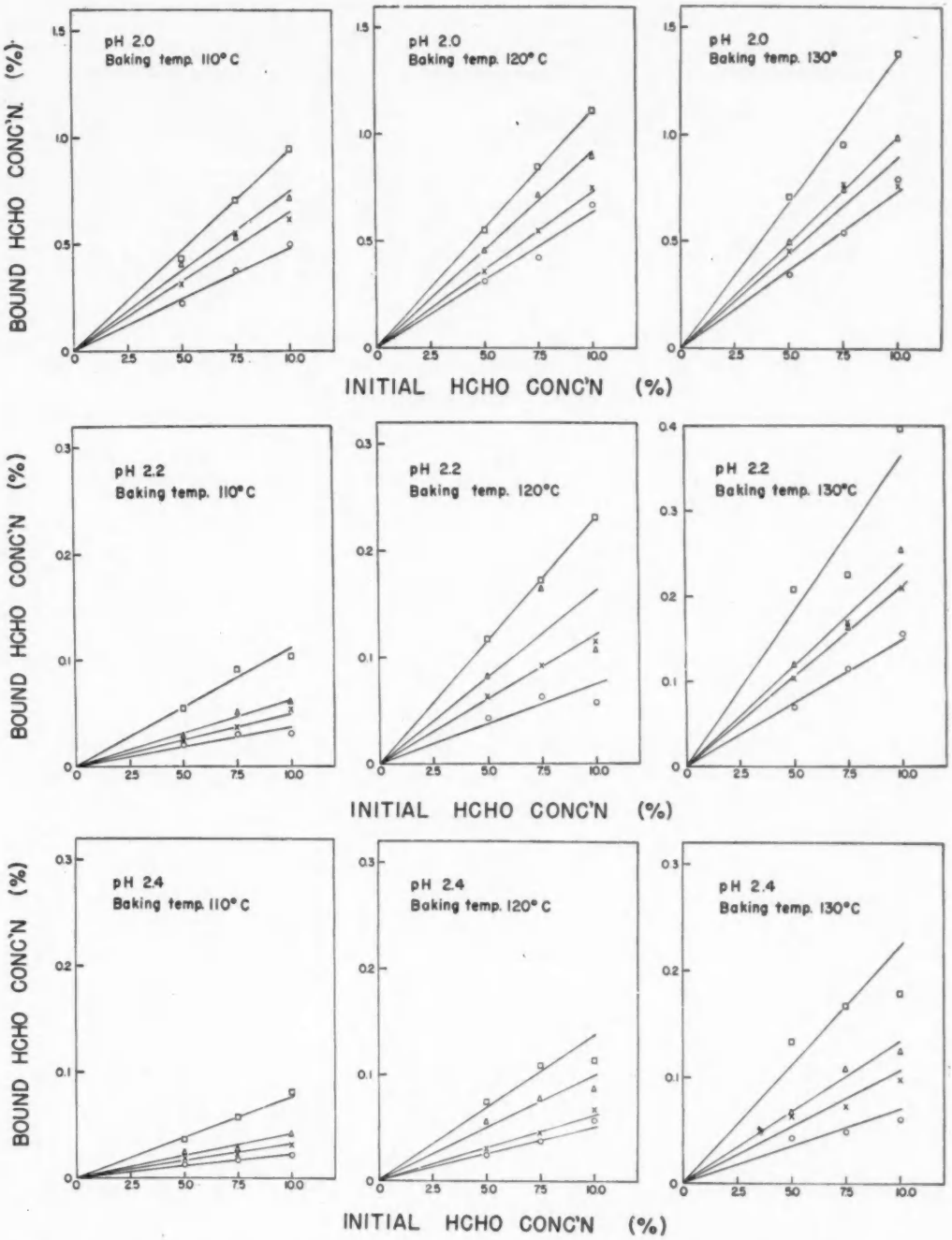



**Fig. 2.** Dependence of bound formaldehyde concentration on initial formaldehyde concentration for cotton (baking period: O—5 min., X—10 min., △—15 min., □—30 min.).

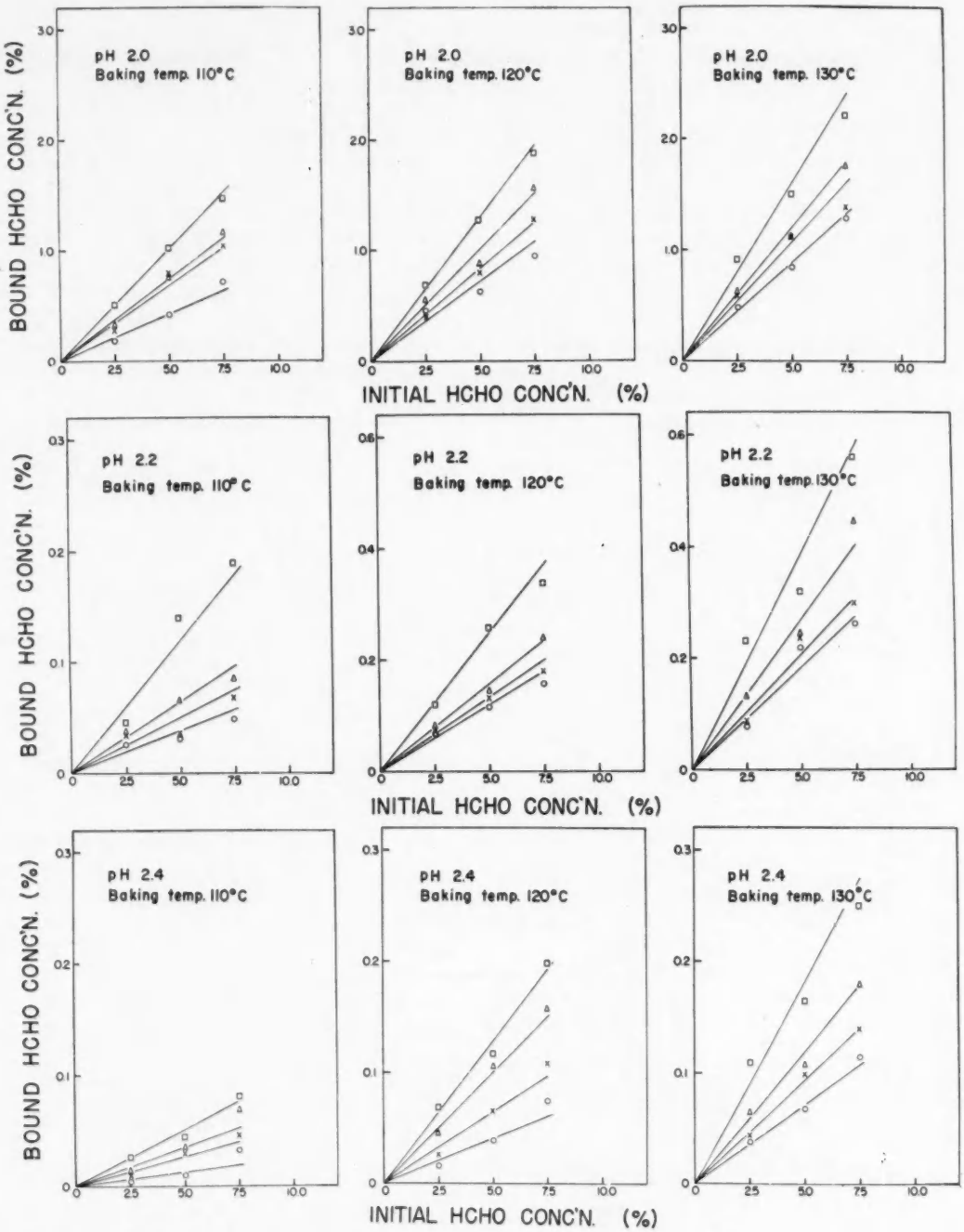



**Fig. 3.** Dependence of bound formaldehyde concentration on initial formaldehyde concentration for Fortisan (baking period: O—5 min., X—10 min., △—15 min., □—30 min.).

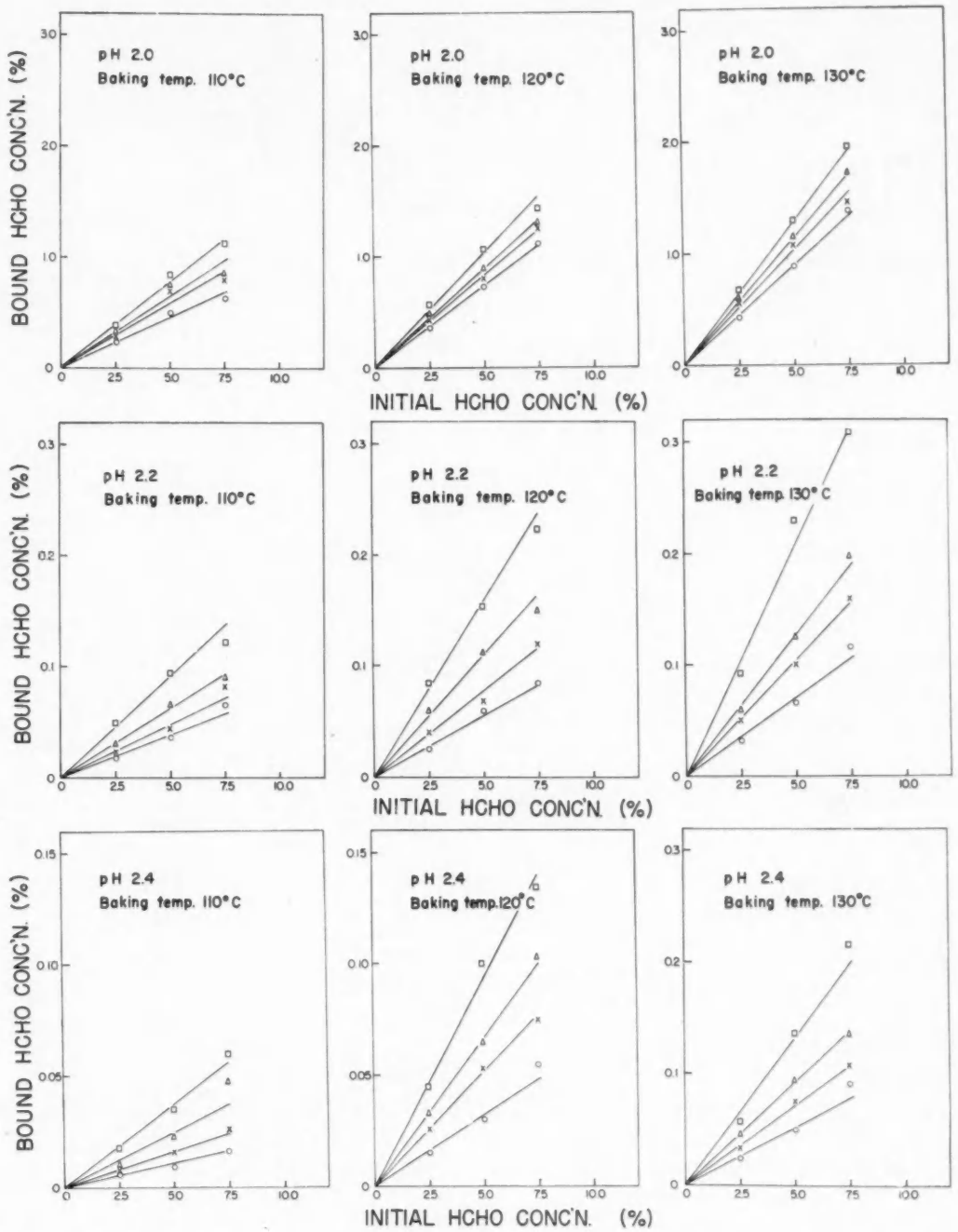



**Fig. 4.** Dependence of bound formaldehyde concentration on initial formaldehyde concentration for rayon (baking period: O—5 min., X—10 min., △—15 min., □—30 min.).

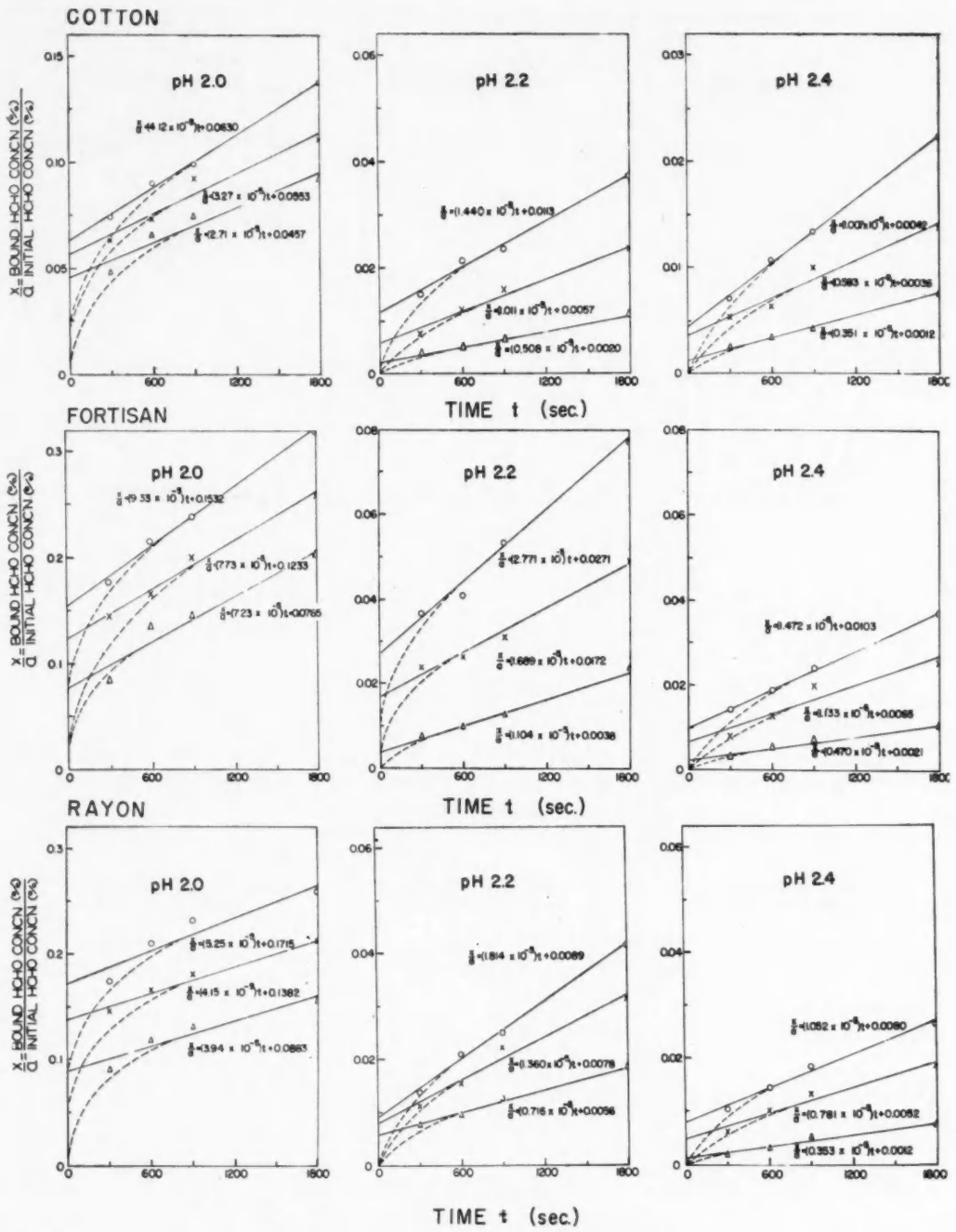



**Fig. 5.** Rate of reaction of cotton, Fortisan, and rayon with formaldehyde (baking temperature: △—110°C., X—120° C., O—130° C.).

**TABLE III. Intercepts of the Rate Plots**

$$C = \left[\frac{\%\text{ bound formaldehyde}}{\%\text{ initial formaldehyde}}\right]_{\text{"0" time}} \times 10^2$$

| pH | 110° C. | 120° C. | 130° C. |
|---|---|---|---|
| | Cotton | | |
| 2.0 | 4.57 ± 0.81 | 5.53 ± 0.66 | 6.30 ± 0.91 |
| 2.2 | 0.195 0.073 | 0.573 0.356 | 1.133 0.376 |
| 2.4 | 0.118 0.054 | 0.363 0.167 | 0.422 0.284 |
| | Fortisan | | |
| 2.0 | 7.65 ± 2.18 | 12.33 ± 2.32 | 15.32 ± 2.84 |
| 2.2 | 0.376 0.371 | 1.724 0.343 | 2.712 0.985 |
| 2.4 | 0.210 0.184 | 0.646 0.341 | 1.025 0.376 |
| | Rayon | | |
| 2.0 | 8.83 ± 1.83 | 13.82 ± 1.21 | 17.15 ± 1.74 |
| 2.2 | 0.557 0.140 | 0.781 0.246 | 0.891 0.274 |
| 2.4 | 0.123 0.086 | 0.515 0.139 | 0.796 0.204 |

When the logarithms of the rate constants of Table II are plotted against the reciprocals of the corresponding absolute temperatures, the straight-line relationships shown in Figure 6 are observed. Activation energies may be obtained from the slopes of these straight lines. To obtain activation energy values that would be associated with a larger number of statistical degrees of freedom than the number available when only three experimental points are involved (one degree of freedom), a procedure was used that led to nine experimental points (seven degrees of freedom) being associated with each energy of activation. Since each of the three $x/a$ values for a single baking time comes from a separate, single experiment, it is possible to calculate three rate constants in place of each of the rate constants listed in Table II. This was done by a process of random selection, wherein any one of these three rate constants was obtained by the method of least squares from single values of $x/a$ randomly selected at each of the four baking times. The mean values calculated from each set of three such rate constants were closely similar to the $k$ values of Table II. The activation energies, obtained from nine points rather than three, are shown in Table IV. Analyses of variance associated with the data of Table IV are given in the Appendix of this paper and will be discussed later.

**TABLE IV. Activation Energies for the Cellulose-Formaldehyde Reaction**

(kcal./mole)

| Fabric | pH of the pad bath 2.0 | 2.2 | 2.4 |
|---|---|---|---|
| Cotton | 6.3 | 15.5 | 15.9 |
| Fortisan | 3.4 | 13.4 | 17.7 |
| Rayon | 4.8 | 14.6 | 16.8 |

## Discussion of Rate Studies

In the treatment of cellulosic fabrics with formaldehyde under acidic conditions as was done in this study, there are two major reactions to be considered. These are the acid hydrolysis of cellulose and the acid-catalyzed formalization process. The formalization process probably involves the formation of a methylene-ether bridge between a molecule of

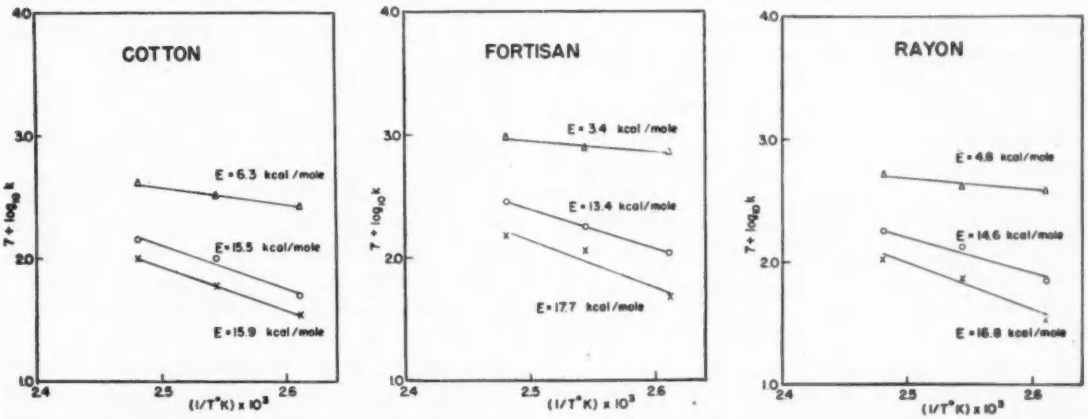



**Fig. 6.** Logarithm of rate constant vs. reciprocal of temperature (°K.) for cotton, Fortisan, and rayon (initial acidity of pad bath: △—pH 2.0, O—pH 2.2, X—pH 2.4).

formaldehyde and two hydroxyl groups of adjacent cellulose chains. The reaction is fundamentally the same as the formation of methylal from methyl alcohol and formaldehyde. Under acidic conditions the reaction takes place readily [22], providing the hydroxyl groups are easily available. In the work reported here, three cellulosic fibers possessing different crystallinities and orientations were subjected to the same conditions of reaction. The observed rates and extents of reaction showed strong dependence on the states of internal order of these different cellulosic fibers. A similar dependence on the state of internal order has been observed for the acid-hydrolysis reaction [12].

It may be seen from Table II that under comparable conditions, the lowest rate constants are found for cotton, the highest are found for Fortisan, and intermediate values are found for rayon. All of the intercepts listed in Table III have values significantly greater than zero. At pH's 2.2 and 2.4, however, these values are relatively small and are probably caused by a small amount of formaldehyde combining with cellulose during the "warm-up" period between the introduction of padded fabric samples into the baking oven and the oven's coming to the desired temperature. At pH 2.0 the corresponding intercept values are much greater and indicate that a considerable amount of formaldehyde has reacted with the cellulose in addition to the small amount of reaction, probably due to the oven "warm-up." Furthermore, the intercept values for Fortisan and rayon at pH 2.0 are about the same and approximately twice the values found for cotton.

According to X-ray determinations of crystallinity in cellulosic fibers made by Hermans and Weidinger [9], cotton is about 70% crystalline and Fortisan and rayon are both about 40% crystalline. Therefore, the amorphous regions in Fortisan and rayon constitute about 60% of the total fiber, which is twice the corresponding value of about 30% for cotton. This information, coupled with that provided by the intercept values of Table III, indicates that at pH's 2.2 and 2.4 the reaction occurs predominantly in the amorphous regions. At pH 2.0, however, the formalization process appears to consist of a combination of a fast (and nearly immediate) reaction in the amorphous regions and a slow one of diffusion of the formaldehyde molecules into the crystalline regions of the fibers where reaction occurs.

Such a viewpoint is supported by the activation energies listed in Table IV. It is apparent that for all three fabrics the reaction carried out at an initial pad-bath pH of 2.0 is markedly different from the reaction at the pH values of 2.2 and 2.4. The details of two-factor (pH and type of fabric) analyses of variance associated with these energies of activation are given in the Appendix. The results of these analyses show that the energies of activation observed for all three fabric types at pH's 2.2 and 2.4 are statistically identical. The actual values observed, ranging from 13.4 to 17.7 kcal./mole, are reasonable ones for the formation of methylene-ether cross-links between adjacent cellulose chains. It may also be shown by the analyses of variance that the activation energies for all three fabric types at pH 2.0 are statistically identical and that these activation energies are very significantly lower than those observed at pH's 2.2 and 2.4. These values of 3.4 to 6.3 kcal./mole are of the magnitude to be expected for a reaction whose rate is diffusion-controlled.

There is no possibility of formulating a quantitative relationship for these experiments between the initial acidity of the pad bath and the rate of reaction. The actual pH of the reaction in the fabric during the baking process has not been determined, and it is under these unknown pH conditions that the reaction actually takes place. The establishment of pH in this study was done primarily to ensure at least a known acidity in the pad bath and thus a qualitative reference. A recent study of Matsuzaki and Yanase [15] indicates that the efficiency of various acid catalysts used for the cellulose-formaldehyde reaction is related to the behavior of the acids upon heating rather than to the pH value of the pad bath. In the case of weak acids, they also found that the extent of reaction could not always be correlated with the dissociation constant of the acid. Accordingly, it seems likely that the great difference observed between the reaction at pH 2.0, where hydrochloric acid was used, and the reactions at pH's 2.2 and 2.4, where hydrochloric acid–potassium acid phthalate buffer systems were used, is caused by the different methods of obtaining acidity. This great difference certainly appears too great to be explained solely by the pH difference between 2.0 and 2.2.

The extents of reaction and the rate constants observed, as discussed previously, are consistent with the proposed reaction mechanisms. Cotton, the most crystalline of the fibers studied, has the least amount of formaldehyde bound to it under all reaction con-

ditions. The rate constants are also the lowest. Fortisan and rayon have approximately the same degree of crystallinity and show approximately the same amount of formaldehyde bound at "zero time." At later baking times, however, particularly at the longest time studied of 30 min., the Fortisan has more bound formaldehyde than rayon, since Fortisan has the higher rate constants in all cases.

There appear to be two possible explanations for Fortisan reacting faster than rayon. One possibility is that when the cellulose chains are fairly well-oriented in the same direction, as they are in Fortisan, they offer a more favorable configuration for cross-linking than is found in rayon. Another possibility is that viscose rayon, being less oriented than Fortisan, may undergo recrystallization to a relatively greater extent during the course of any acid hydrolysis accompanying the reaction with formaldehyde. Any recrystallization would, of course, hinder reaction with formaldehyde. It is believed that after cellulose chains are broken by acid hydrolysis in the accessible regions, there results an increased mobility of the broken chain ends, which induces further crystallization than that already present. The phenomenon of recrystallization was first suggested by Ingersoll in 1946 [14] as an explanation for certain of his X-ray measurements. His findings have since been substantiated by the work of a number of other investigators [1, 10, 13]. Howsmon [13] has shown that recrystallization occurs during acid hydrolysis rather than during drying after hydrolysis and that recrystallization in native cellulose fibers is less than in regenerated fibers. In the case of ramie, a native fiber of high crystallinity and orientation, Hermans and Weidinger [10] have shown that the fraction of crystalline material present undergoes no change during acid hydrolysis. These two suggested explanations are not mutually exclusive. It would seem, however, that the argument involving a difference in the recrystallization of Fortisan and rayon during hydrolysis is more consistent with the proposed reaction mechanism.

## X-Ray Diffraction Studies

To obtain further information on the reaction mechanisms discussed in the previous section, X-ray diffraction patterns of variously treated fibers were obtained and examined. From X-ray diffraction patterns, two major parameters related to the crystalline components of the fibers can be determined, namely, orientation distribution and lateral order. If hydroxyl groups in the crystalline regions were involved in cross-linking, it is likely that the cellulose chains would be twisted and turned about their original positions by the newly formed cross-links, resulting in a wider orientation distribution. The formation of cross-links inside the ordered regions would probably disturb the alignment of the chains and distend the orderly structure, resulting in a lower degree of order. If the reaction were completely confined to the amorphous regions, no change in the diffraction pattern should be observed.

For each of the three cellulosic fiber types, five diffraction patterns were obtained, one for each of the treatments as follows:

| Sample | Treatment description |
|---|---|
| a | Control (original fabric, untreated) |
| b | HCHO-treated at pH 2.0 (7.5% HCHO, 110° C., 30 min.) |
| c | Acid-treated at pH 2.0 (0.0% HCHO, 110° C., 30 min.) |
| d | HCHO-treated at pH 2.2 (7.5% HCHO, 110° C., 30 min.) |
| e | Acid-treated at pH 2.2 (0.0% HCHO, 110° C., 30 min.) |

In each case the specimen was a bundle of fifty fibers teased from the yarns in the fabric. The fibers were lined up in parallel positions in the bundle.

Flat-plate X-ray diffraction patterns of these fiber bundles were taken with a North American Philips X-ray diffraction apparatus, using Ni-filtered Cu-K$\alpha$ radiation and a specimen-to-film distance of 3 cm. The tube operating conditions were 15 milliamperes and 30 kilovolts. After an exposure time of 4 hr. in each case, the films were developed under controlled conditions.

### *Cotton*

The diffraction patterns of the cotton samples are shown in Figure 7. In cotton, whose pattern is that of native cellulose or "cellulose I," the diffraction ring corresponding to the 002 interference is seen as two sickle-shaped arcs on opposite sides of the center of the diffraction pattern. When all the diagrams are compared, it may be seen that the pH 2.0 formaldehyde-treated sample, Figure 7*b*, has the widest angle subtended by the arc due to this 002 interference. All the other treated samples do not differ noticeably from one another or from the con-

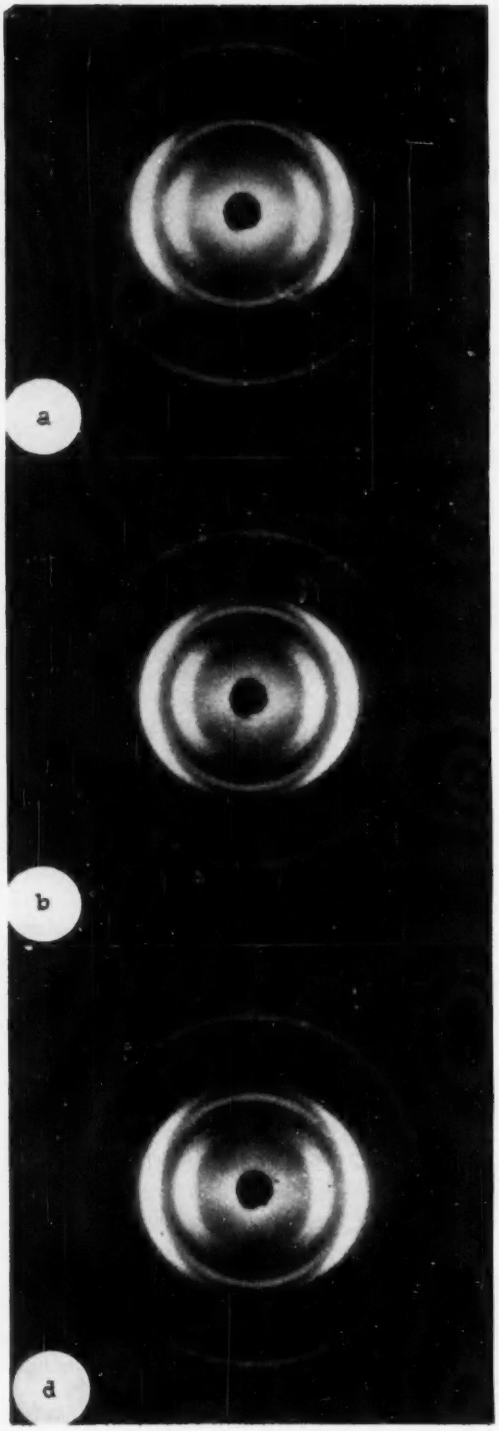



Fig. 7. COTTON
(baked at 110° C, 30 min.)

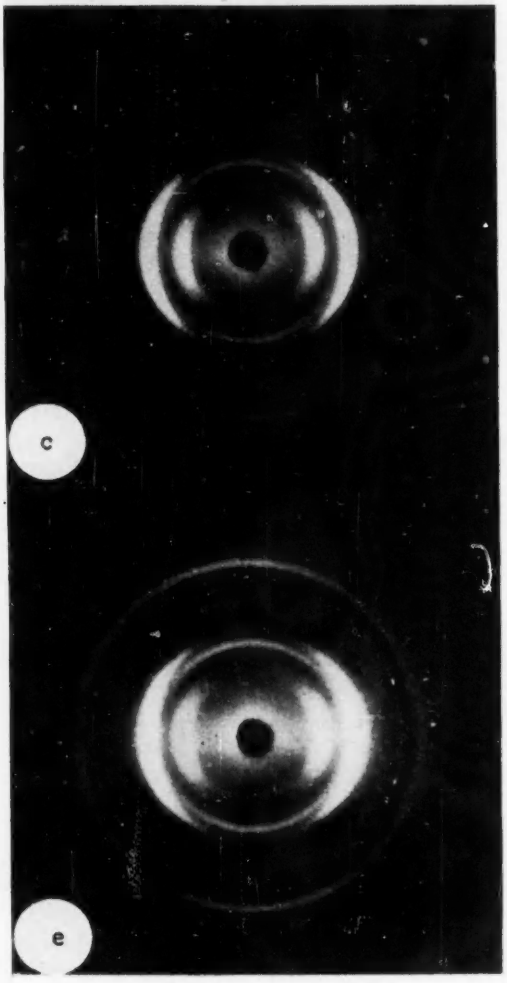
a. Original, untreated

b. HCHO treated
(pH 2.0, HCHO 7.5%)

c. Acid treated
(pH 2.0, HCHO 0.0%)

d. HCHO treated
(pH 2.2, HCHO 7.5%)

e. Acid treated
(pH 2.2, HCHO 0.0%)



trol. A similar situation is observed for the arcs corresponding to the associated interferences of the 101 and 10$\bar{1}$ planes, the pH 2.0 formaldehyde-treated sample having an appreciably longer arc than the original and all the other treated samples.

*Fortisan*

The Fortisan diffraction patterns are shown in Figure 8. Fortisan is a very highly oriented fiber, and correspondingly its diffraction pattern, that of regenerated cellulose or "cellulose II," exhibits very short arcs. The pH 2.0 formaldehyde-treated sample, Figure 8*b*, stands out with marked difference from the untreated sample, Figure 8*a*. The associated 10$\bar{1}$ and 002 interferences have their arcs greatly extended by the formaldehyde treatment at pH 2.0, indicating that the orientation of the corresponding crystalline planes has been disturbed and reduced by the treatment. A similar pronounced increase in arc length is observed for the 101 interference.

Disorientation and disturbance of the crystallites are also noticeable when the sample treated with formaldehyde at pH 2.2, Figure 8*d*, is compared with the control. But the pH 2.2 acid-treated sample, Figure 8*c*, shows about the same effect, indicating that the disturbance arises more from the acid treatment than from the cross-linking. The same comparison of the pH 2.0 formaldehyde-treated sample, Figure 8*b*, with the pH 2.0 acid-treated sample, Figure 8*c*, and the control, Figure 8*a*, shows that at this higher acidity some disturbance is also caused by the acid alone, but it is very much less than in the case of the formaldehyde-treated sample. The effect of cross-linking is much more pronounced at pH 2.0.

*Rayon*

The diffraction patterns for rayon are shown in Figure 9. Rayon, another regenerated cellulose fiber containing primarily "cellulose II" crystals, has a much lower degree of orientation than Fortisan. The diffraction patterns of Figure 9 show diffuse rings and considerable "amorphous backgrounds." An indication of the orientation present may be obtained from comparing equatorial and polar intensities of the 10$\bar{1}$–002 doublet. The contrast appears to be greater in the case of the control sample, Figure 9*a*, than in the case of the pH 2.0 formaldehyde-treated sample, Figure 9*b*. Because of the background, it is very difficult, if not impossible, to make any estimate of orientation based on the 101 interference. Careful examination suggests that the pH 2.0 acid-treated sample, Figure 9*c*, has a higher orientation than the pH 2.0 formaldehyde-treated sample, Figure 9*b*. It does not seem possible to make any comments regarding relative orientations in the cases of the samples treated at pH 2.2, Figures 9*d* and 9*e*.

In summary, it would appear that the proposed reaction mechanisms are partially verified by these X-ray diffraction studies. The diffraction patterns of the fibers treated at pH 2.0 indicate that the crystallites have been disturbed and disoriented by formaldehyde cross-linking. This cross-linking does not appear to have such effects at pH 2.2. The evidence is most pronounced in the case of Fortisan, fairly positive in the case of cotton, but inconclusive in the case of rayon.

## Conclusions

1. The course of the cellulose-formaldehyde reaction, as carried out under the experimental conditions of this study, is found to be the same for three different cellulosic fibers: cotton, Fortisan, and viscose rayon.

2. When the initial pH values of the pad bath are 2.2 and 2.4, the reaction rate appears to be controlled by a process that takes place primarily in the amorphous regions of the fibers with an activation energy of 13.4–17.7 kcal./mole. This reaction appears to be the production of methylene-ether cross-links between adjacent cellulose chains. At an initial pad-bath pH of 2.0, there is indication of a very rapid reaction in the amorphous regions, accompanied and followed by further reaction in the crystalline regions, the latter process being rate-determining and controlled by diffusion. This diffusion-controlled reaction has an activation energy of 3.4–6.3 kcal./mole. This effect is probably due to the use of a different source of acidity for the pH 2.0 experiments. The proposed reaction mechanisms appear to be verified by X-ray diffraction studies.

3. The rate and extent of reaction depend on the state of internal order of the cellulosic material. Cotton reacts slower and to a less extent than either Fortisan or viscose rayon. The latter two fibers have about the same degree of crystallinity, but the reaction with Fortisan is more rapid than with viscose rayon. Two possible explanations are (*a*) that the higher orientation of Fortisan may facilitate the

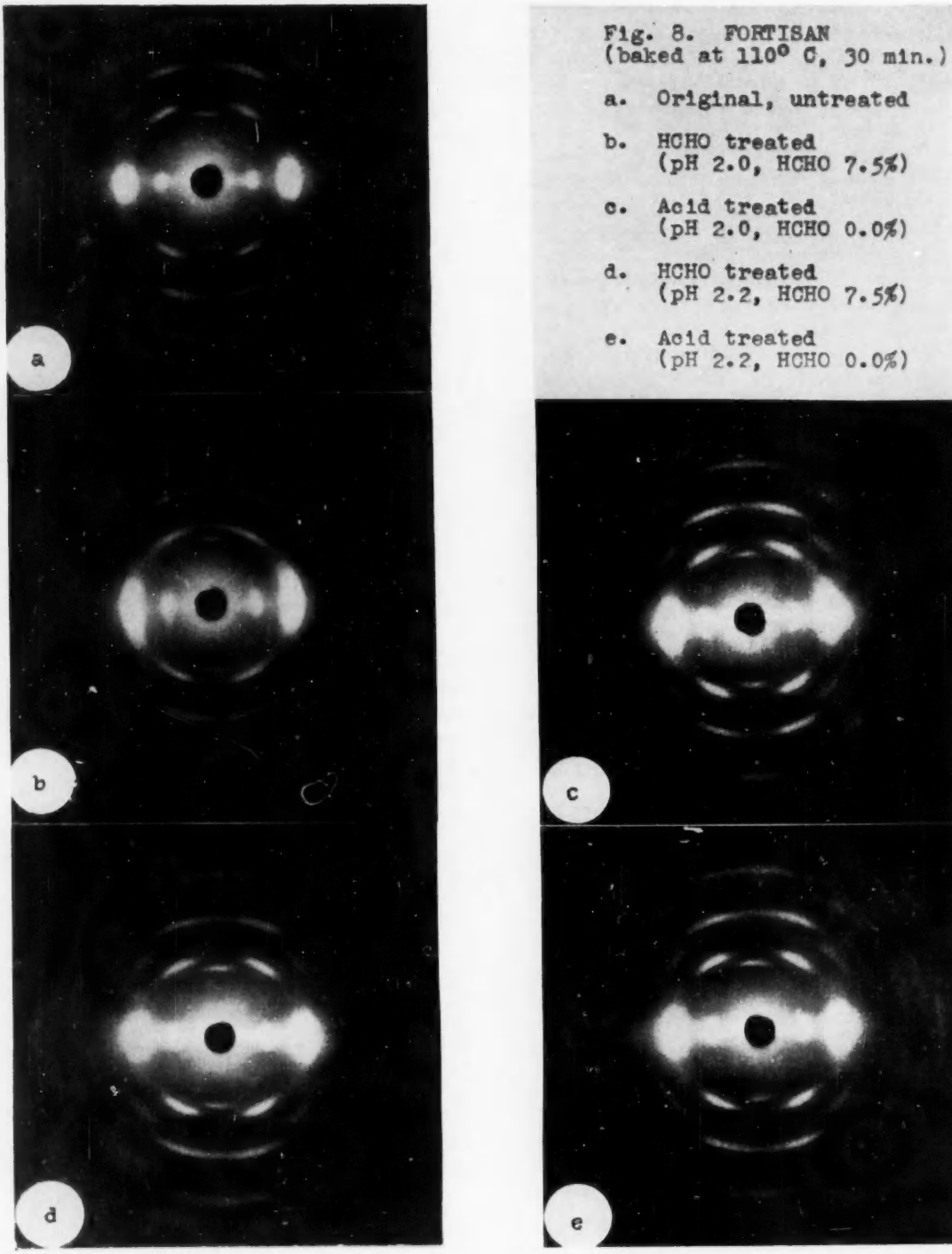



Fig. 8. FORTISAN
(baked at 110° C, 30 min.)

a. Original, untreated

b. HCHO treated
(pH 2.0, HCHO 7.5%)

c. Acid treated
(pH 2.0, HCHO 0.0%)

d. HCHO treated
(pH 2.2, HCHO 7.5%)

e. Acid treated
(pH 2.2, HCHO 0.0%)

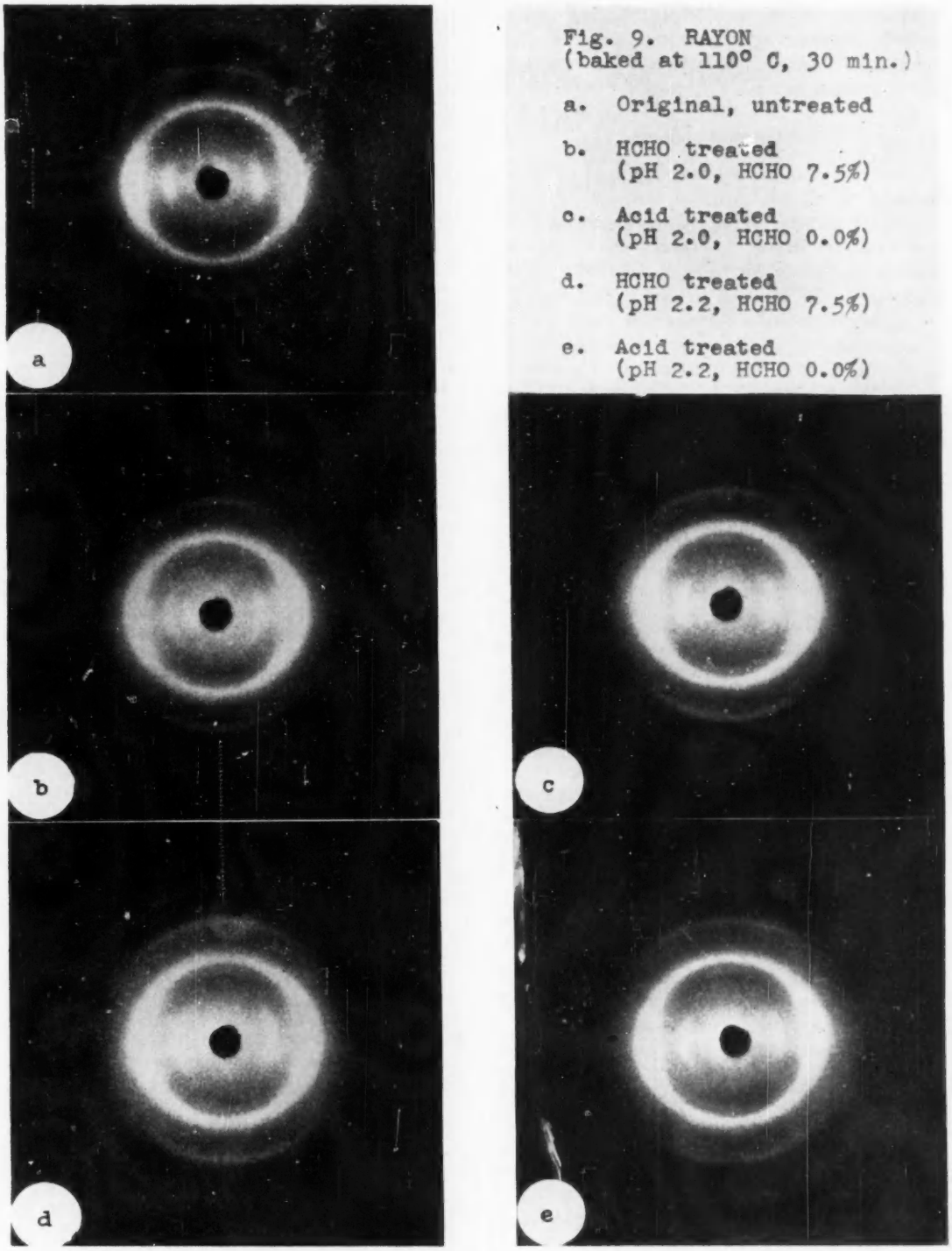



Fig. 9. RAYON
(baked at 110° C, 30 min.)

a. Original, untreated

b. HCHO treated
(pH 2.0, HCHO 7.5%)

c. Acid treated
(pH 2.0, HCHO 0.0%)

d. HCHO treated
(pH 2.2, HCHO 7.5%)

e. Acid treated
(pH 2.2, HCHO 0.0%)

cross-linking process or (*b*) that during acid hydrolysis accompanying the cross-linking, recrystallization occurs, and rayon may have a relatively higher rate of recrystallization.


## Acknowledgments

This work was carried out as a part of Textile Research Institute's General Research Program. One of the authors (H. K. Woo) thanks the Goodyear Tire and Rubber Company for its fellowship grant in support of this research. Thanks are due Professor J. C. Whitwell for his advice regarding the statistical aspects of the work, E. Crystal for his assistance in some of the statistical calculations, and H. W. Lambert for his construction of the baking oven. The assistance of G. D. Mallory of the Goodyear Tire and Rubber Company in supplying the cotton and Fortisan fabric samples is gratefully acknowledged. The viscose rayon fabric was kindly supplied by J. A. Woodruff of the American Viscose Corporation.


## Appendix

The results of the analyses of variance associated with the activation energies listed in Table IV have been discussed previously in the section of this paper titled "Discussion of Rate Studies." The analyses were performed upon the least-squares slopes obtained when logarithms (to base 10) of the rate constants were plotted against the reciprocals of the corresponding absolute temperatures. Since the activation energies are obtained by the multiplication of these slopes by a constant, the results of performing analyses of variance on the slopes would be the same as performing the analyses on the activation energies.

The analysis of variance for all three fabric types at the three pad-bath pH values is given in Table V.

**TABLE V. Analysis of Variance for pH's 2.0, 2.2, and 2.4**

| Effect | Sums of squares | d.f. | Mean squares | F |
|---|---|---|---|---|
| pH | 11,532,275 | 2 | 5,766,137 | 12.79* |
| Fabric | 81,806 | 2 | 40,903 | 0.09 |
| pH×fabric | 390,977 | 4 | 97,744 | 0.22 |
| Replication | 28,402,164 | 63 | 450,828 | |

* Effect is significant at better than the 0.1% level.

The analysis of variance for all three fabric types at only pH's 2.2 and 2.4 is given in Table VI.

**TABLE VI. Analysis of Variance for pH's 2.2 and 2.4**

| Effect | Sums of squares | d.f. | Mean squares | F |
|---|---|---|---|---|
| pH | 368,306 | 1 | 368,306 | 0.72 |
| Fabric | 101,044 | 2 | 50,522 | 0.10 |
| pH×fabric | 82,846 | 2 | 41,423 | 0.08 |
| Replication | 21,603,032 | 42 | 514,358 | |

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# The Reaction of Formaldehyde with Cellulosic Fibers

## Part II: Mechanical Behavior[1]

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### Abstract

The effects of an acid-catalyzed formaldehyde treatment on such mechanical properties as breaking strength and crease recovery have been determined for three cellulosic fabrics: cotton, Fortisan, and viscose rayon. Samples of these materials, treated under a selected set of conditions, were compared with three "controls": untreated fabric, fabric treated with distilled water under the conditions of the formaldehyde treatment, and fabric treated with the acid solution used in the formaldehyde treatment under the same conditions. The two-dimensional load-elongation behavior of the fabrics was investigated, and comparisons were made with the results of corresponding one-dimensional tests. The mechanical properties of single fibers and yarns taken from the variously treated fabrics were also measured.

In general, cotton fabrics showed a deterioration in mechanical properties due to formaldehyde cross-linking with respect to the acid-treated control, while correspondingly, Fortisan and viscose rayon were improved by such treatment. In the case of cotton fibers and fabrics, it was found that the formaldehyde treatment had reduced the fiber and fabric elastic moduli with respect to the acid-treated control, although the formaldehyde treatment had also reduced correspondingly the fiber and fabric breaking strains. The deterioration in mechanical properties caused by hydrochloric acid was most marked in the case of Fortisan. It was found that generally the properties of single fibers, yarns, and fabrics are closely related.

The improvement in crease recovery caused by the formaldehyde treatment was greatest for cotton, less for Fortisan, and least for viscose rayon. These different responses to the cross-linking reaction appear to be related to the different states of internal order of the three cellulosic fibers. Crease-recovery tests carried out on all the variously treated fabrics showed that marked improvements in crease recovery were usually obtained only with those treated at an initial pad-bath pH of 2.0, which indicates that a high degree of cross-linking of the hydroxyl groups in the amorphous regions of the fibers is necessary to achieve high degrees of crease recovery.

### Introduction

In Part I of this series of two papers, studies were reported of the rate and mechanism of the reaction of formaldehyde with cellulosic fibers [19]. It was mentioned in that paper that an important purpose of studying the formaldehyde-cellulose reaction would be to determine the effects of the formaldehyde treatment on the mechanical behavior of the various fibers. This paper is concerned with reporting and discussing such effects.

Cellulosic fabrics are treated with formaldehyde or with textile-finishing resins containing formaldehyde to improve their dimensional-stability and crease-recovery characteristics. It is well known that the improvement in these properties is often accompanied by decreases in such mechanical proper-

[1] This paper is based upon part of a dissertation submitted by H. K. Woo in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

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ties as fabric breaking strength and tear strength. The copious literature on this subject up to 1949 has been reviewed, with special emphasis on cotton, by Buck and McCord [3]. More recently, a thorough review of the mechanical behavior of cellulosic fibers has been given by Wakeham [17].

In 1948, Gruntfest and Gagliardi [7] showed that relatively low concentrations of formaldehyde (2% on weight of fabric) produced more improvement in crease recovery on cotton than on rayon, whereas at higher concentrations (10% o.w.f.) the improvement was about the same for cotton and rayon. In studying viscose rayon yarns, they found that formaldehyde treatment increased the elastic modulus and the elastic recovery from 2% extension, decreased the breaking extension, and had little effect on breaking strength. In another paper in 1949 [8], they showed that there was a good correlation between fabric crease recovery and yarn strain recovery when viscose rayon filament yarns were treated with formaldehyde. More extensive studies in this field were reported by Gagliardi and Gruntfest in 1950 [6]. In addition to reporting further measurements demonstrating a correlation between the elastic recovery of yarns and the crease recovery of the corresponding viscose rayon fabrics treated with formaldehyde, they showed that formaldehyde (10% o.w.f.) caused greater breaking strength losses on cotton fabrics than on rayon. When urea-formaldehyde and melamine-formaldehyde finishing resins (15% o.w.f.) were used, they found that cotton fabrics suffered lower breaking strength losses than were caused by formaldehyde treatment and that in the case of rayon, the amine-formaldehyde resin treatment actually improved the breaking strength over that of the control fabric.

Later in 1950, Beste and Hoffman [2], in a study of the extensional resilience of many different fibers, showed that there was generally good correlation between the elastic-recovery properties of single fibers and the crease-recovery characteristics of fabrics made from them. They found that the best correlation was usually obtained when the elastic recovery was determined for extensions of 3% and 5% and that single-fiber work recovery (ratio of energy recovered to energy expended in stretching) correlated a little better with fabric crease recovery than did the corresponding elastic recovery from extension. These workers also pointed out the importance of moisture content with respect to fiber elastic recovery. While synthetic fibers such as nylon 66 and Dacron [5] are relatively insensitive to humidity changes, they showed that the elastic recovery of regenerated fibers prepared from protein (zein fibers) or from cellulose (rayon) decreases with increasing relative humidity. Hamburger, Platt, and Morgan [9] have analyzed the performance of textiles from an engineering standpoint and have stressed the fact that the average strain on most textile fabrics during use is of relatively low order and considerably less than that required for rupture. The results of their measurements led them to conclude ". . . that high immediate elastic deflection at low average tensile strains is an important fiber property in determining the crease recovery of fabrics."

Cameron and Morton [4] suggested in 1948 that urea-formaldehyde resins impart crease recovery to viscose rayon fabrics by cross-linking adjacent cellulose chains. They proposed that the greater part of the resin material was deposited in the amorphous regions of the rayon fibers and that the changes in fiber properties brought about by resin treatment were caused by the small fraction of this deposited material involved in cross-linking. In 1950, Gagliardi and Gruntfest [6] advanced the theory that formaldehyde improves the crease recovery of cellulosic fabrics by cross-linking cellulose chains.

An extensive investigation of how textile-finishing resins impart wrinkle recovery to cotton and rayon fabrics was reported by Cooke, Dusenbury, Kienle, and Lineken [5] in 1954. These workers confirmed earlier findings and showed that improvement in fabric crease recovery is caused by an increase in single-fiber elastic recovery, this increase being carried over into the yarns and fabrics constructed from the fibers. They also showed that the ability of a fabric to recover from creasing is more important than its ability to resist creasing and that, in the cases of urea- and melamine-formaldehyde resins applied to cotton, the resin is most likely deposited in the amorphous regions of the cellulose. From a study of the infrared absorption spectra of resin-treated cellophane, Cooke *et al.* [5] concluded that crease recovery is caused primarily by chemical reaction within the cellulose fiber, which cross-links adjacent cellulose chains. They postulated that this cross-linking prevents irreversible slippage of adjacent cellulose chains during fiber extension, thereby reducing permanent set and increasing elastic recovery. In a study of the effect of formaldehyde

[5] Du Pont polyester fiber.

treatment on the elastic moduli of rayon fibers in extension, bending, and torsion, Kärrholm [12] in 1955 reported that formaldehyde treatment increased the immediate elastic deflection and decreased the secondary creep components of fiber deformation, with primary creep only slightly affected. Her findings in this regard were closely similar to those of Cooke *et al.*

Most recently, Steele and Giddings [16] have considered the reaction of cellulosic fibers with dimethylol- and monomethylolureas. They have proposed that dimethylolurea forms cross-links of relatively short length between adjacent cellulose chains, whereas the monomethylol compound reacts only to form side-chains with the cellulose. Their work indicates that the cross-linking reaction is more effective for cotton than for rayon at low resin concentrations (up to 5–6% o.w.f.) and that this is due to cotton's having the lower chemical accessibility. In a study they made of the improvement in crease recovery caused by varying amounts of dimethylolurea applied to the fabrics, it was found that at comparable resin concentrations, cotton was most improved, Fortisan was less improved, and viscose rayon was improved the least.

As mentioned earlier, the objective of this paper is to determine the effects of formaldehyde treatment on the mechanical behavior of three different cellulosic materials: cotton, Fortisan, and viscose rayon. This main objective might be subdivided into three parts:

(1) To supplement the rate and mechanism studies [19] in elucidating the nature of the reaction of formaldehyde with three cellulosic fibers of different states of internal order.

(2) To gain information on fiber-yarn-fabric relationships, by determining how the modifications in single-fiber behavior caused by formaldehyde treatment are carried through to the corresponding yarns and fabrics.

(3) To gain information in regard to how formaldehyde treatment affects the two-dimensional force vs. extension properties of fabrics made with fibers of different states of internal order. The two-dimensional load-elongation tester used for this purpose [15] is designed to supply more complete information on the force-extension properties of a woven fabric than that obtainable from conventional one-dimensional tests.

The studies were carried out in two sections. Section A consists of a cursory examination of the breaking strengths, breaking extensions, and crease recoveries of all the fabrics resulting from each set of reaction conditions described in the Part I paper [19]. These screening tests permitted the selection of a set of optimum treatment conditions under which significant improvements in wrinkle-recovery characteristics are obtained without excessive losses in breaking strengths.

Section B consists of a detailed study of the mechanical properties of the fabrics, yarns, and fibers under the optimum conditions of formaldehyde treatment selected on the basis of the results reported in Section A. These properties of the formaldehyde-treated samples are compared with the corresponding properties of (*a*) the original, untreated samples, (*b*) samples treated with distilled water under the same conditions, and (*c*) samples treated with the acid solution used to give the same pH as that of the formaldehyde treatment under the same conditions.

For convenience, a standard notation was adopted and used in all the figures. The notation should be clear from the following illustrations:

COw Cotton, Original untreated sample, warp
FWf Fortisan, Water-treated sample, filling
RAw Rayon, Acid-treated sample, warp
CFf Cotton, Formaldehyde-treated sample, filling

## Apparatus and Methods

All tests in the followng paragraphs were carried out on conditioned samples in a conditioned room maintained at 65% ± 2% R.H. and 70° ± 2° F.

### *Single-Fiber Tests*

Force vs. extension curves to rupture were obtained on single fibers with the use of the Instron testing machine [11]. The fibers, after removal from yarns taken from the fabrics and subsequent relaxation, were tested at a gauge length of approximately 0.5 in. (exact gauge length in each case is measured to better than 0.01 in.) and at a crosshead speed of 0.05 in./min. The fiber cross-sectional area was measured during the tensile test with a vibroscope attached to the Instron machine, a technique which has been developed at Textile Research Institute [14, 18]. The load-elongation curves thus obtained were analyzed to obtain the following properties: breaking stress in g./cm.$^2$, breaking strain in per cent of initial length, elastic modulus in g./cm.$^2$ for 100% extension, and toughness (total area under the load-elongation curve) in g./cm.$^2$—that is, the energy to break per unit of initial volume of fiber.

*Yarn Tensile Tests*

Yarn samples taken from the fabrics were tested on the Instron machine at a 3.0-in. gauge length and at a crosshead speed of 0.5 in./min., with precautions taken to avoid untwisting of the yarns prior to testing. The resulting load-elongation curves were analyzed in the same manner as in the case of single fibers, and the corresponding properties were calculated: breaking load, breaking strain, elastic modulus, and toughness. In this instance, however, the appropriate properties were not normalized to the yarn cross-sectional areas.

*Fabric Tensile Tests*

Conventional one-dimensional fabric tests were also made on the Instron machine with samples 6 in. long × 3 in. wide. When filling threads were being tested, the filling dimension of the sample was 6 in. The jaw separation was 3 in. and the jaw speed 0.5 in./min. The jaws were designed to grab a 2-in. width of the fabric sample and were 1 in. in depth. It should be noted that this test procedure does not conform to the ASTM standards for either a grab test or a strip test [1]. The test employed here was designed specifically to furnish a better basis for comparison of results with those of the two-dimensional test which has a nonvariable initial jaw separation of 3 in. The following properties were obtained from the load-extension curves: breaking load, breaking strain, elastic modulus, and toughness. Here, as in the case of the yarns, no attempt was made to normalize the appropriate quantities to cross-sectional area.

The two-dimensional fabric tests were carried out according to the techniques described by Reichardt, Woo, and Montgomery [15]. The testing device these workers described has been used by Woo and Montgomery [20] to determine the effects of fabric construction and fiber type on the two-dimensional load-elongation properties of fabrics. The fabric samples used in these tests were 6 in. × 6 in. The jaw widths were 2 in., and the initial jaw separations were 3 in. in both directions. The rate of jaw movement, controlled by the crosshead speed, was 0.5 in./min. The deflection measuring point of the internal strain-sensing device [15] was located at a distance 0.9 in. below the center line of the sample.

*Fabric Crease-Recovery Tests*

The Monsanto Wrinkle Recovery Tester [13] was employed for these measurements.

*Limitations of Tests and Conditions*

The studies of mechanical behavior as described above are far from complete and ideal. An important omission is the study of the "wet" properties of the formaldehyde-treated fibers, yarns, and fabrics. Dimensional stability of the treated fabrics is a pertinent fabric property that has not been measured. The two-dimensional testing device, as it is, has been arbitrarily set up so that the rates of jaw separation in the vertical and horizontal directions are equal. Undoubtedly, there are situations where it would be desirable to have the ratio of the two rates of jaw separation other than unity. It should be further recognized that it would be desirable to control the rates of extension in the warp and filling directions rather than the rates of jaw separation.

## Section A: Screening Test to Determine Optimum Conditions of Treatment

The tensile tests of these screening experiments were carried out only on fabrics, using the conditions for the one-dimensional tests as set forth in the previous section. Two tests, both in the warp direction, were made for each untreated sample and the samples treated under every set of reaction conditions described in the studies on reaction mechanism [19]. The wrinkle-recovery tests were also made on warp samples. Only one test was made for each untreated and treated sample. The data are given in Tables III–VI of the Appendix.

The individual values so obtained are, of course, quite limited in statistical meaning. But, taken as a group at one pH, one temperature, or one initial concentration of formaldehyde, they reveal general trends. In all cases, the most significant variable appears to be the pH value of the treating bath. Examination of the data of both the tensile tests and the wrinkle-recovery tests suggests that the samples can be grouped into two distinctly different classes, those treated at an initial pH of 2.0, and those treated at pH 2.2 and 2.4. Marked improvement in wrinkle recovery is obtained only with fabrics treated at pH 2.0. Coupled with this improvement in wrinkle recovery is a considerable decrease in breaking elongation. A severe loss in tensile strength (approximately 60%) is observed in the cases of cotton and Fortisan, while the loss in the case of viscose rayon is not as great (approximately 15%).

As pointed out in Part I [19], the pH 2.0 treat-

ment probably involves a very rapid reaction of considerable extent in the amorphous region, followed by further reaction in the same region, and subsequently some reaction in the crystalline region. It appears, therefore, that effective improvement in wrinkle recoverability is attained only when extensive cross-linking has taken place between molecular chains in the amorphous regions. Since the amorphous regions of the fiber structure are mainly responsible for the deformable mechanical behavior, it is not surprising that loss in tensile strength and decrease in extensibility also occur in substantial amounts only when extensive reaction has occurred in those regions.

As the treatments made at pH 2.2 and 2.4 do not appreciably improve the wrinkle recovery, it was necessary to choose a set of optimum conditions with pH 2.0, despite the undesirable loss in tensile strength and extensibility. In the group of data obtained at pH 2.0, it can be generalized that higher temperature, higher concentration of formaldehyde applied, and longer baking period yield products of higher wrinkle recoverability, lower tensile strength, and lower extensibility (conditions favoring high degree of cross-linking).

A more detailed examination of the data indicates that the effect of baking temperature on wrinkle recovery is not very great, while the effects of increasing the baking time and the initial concentration of formaldehyde applied are easily observed. The tensile tests, on the other hand, show that the decreases in strength and extensibility are greater with increase in baking temperature than with increase of initial formaldehyde concentration or increase in baking time. In making a selection of the optimum conditions, therefore, it was decided to choose the lowest temperature, the longest baking period, and the highest initial formaldehyde concentration common to the three fabrics. These conditions were:

| | |
|---|---|
| pH of treating bath | 2.0 |
| Baking temperature | 110° C. |
| Baking period | 30 min. |
| Initial HCHO concentration | 7.5% |

This combination was selected to yield treated fabrics of enhanced wrinkle recoverability but with relatively low losses in tensile strength and extensibility. The reproducibility of this formaldehyde treatment is shown in Table I.

**TABLE I. Reproducibility of Formaldehyde Treatment**

[Fabric padded with solution containing 7.5% HCHO at pH 2.0 (0.01 *M* HCl, 0.05 *M* KCl); baked 30 min. at 110° C.]

| Value | Bound HCHO (% on weight of treated sample) | | |
|---|---|---|---|
| | Cotton | Fortisan | Rayon |
| Mean* | 0.66 | 1.43 | 1.07 |
| 95% confidence level of mean | ±0.059 | ±0.126 | ±0.043 |

* Based on seven different samples for cotton and rayon, and six for Fortisan.

## Section B: Experiments with Samples Treated under Optimum Conditions

### 1. *Stress-Strain and Load-Strain Relationships*

Typical stress-strain curves for the single fibers are plotted in Figure 1. These are not average curves but represent in each instance an actual curve whose parameters are nearest to those that would be obtained from average data. Code symbols indicating the fiber by the first letter, the treatment by the second letter, and warp or filling by the third letter have been used in accord with the examples given in the Introduction.

It is first to be noted that the effect of soaking in water and baking is not very great for any of the fibers, although in most cases the stress-strain curve is lowered slightly, i.e., the stresses are lower for all strains in most cases of the water-treated fibers. The effect of acid is much more pronounced in the cases of cotton and Fortisan. The severe drop in breaking stress and extensibility for the cotton fibers due to acid hydrolysis has been observed, and the fact that the effect is much less with the viscose rayon fibers was also to be expected from the work of other experimenters in this field.

The very severe drop in breaking stress and extensibility in the case of Fortisan was surprising. It might be well to keep this extreme acid sensitivity of Fortisan in mind when it is used with a neoprene coating for lighter-than-air aircraft fabrics. Under certain conditions, neoprene is known to generate hydrogen chloride which could very well attack the Fortisan at the temperatures reached at moderate altitudes with high intensity of solar radiation.

It appears that the optimum conditions of treatment chosen for these experiments were ideal to demonstrate the very different effects of formaldehyde upon the properties of native and regenerated

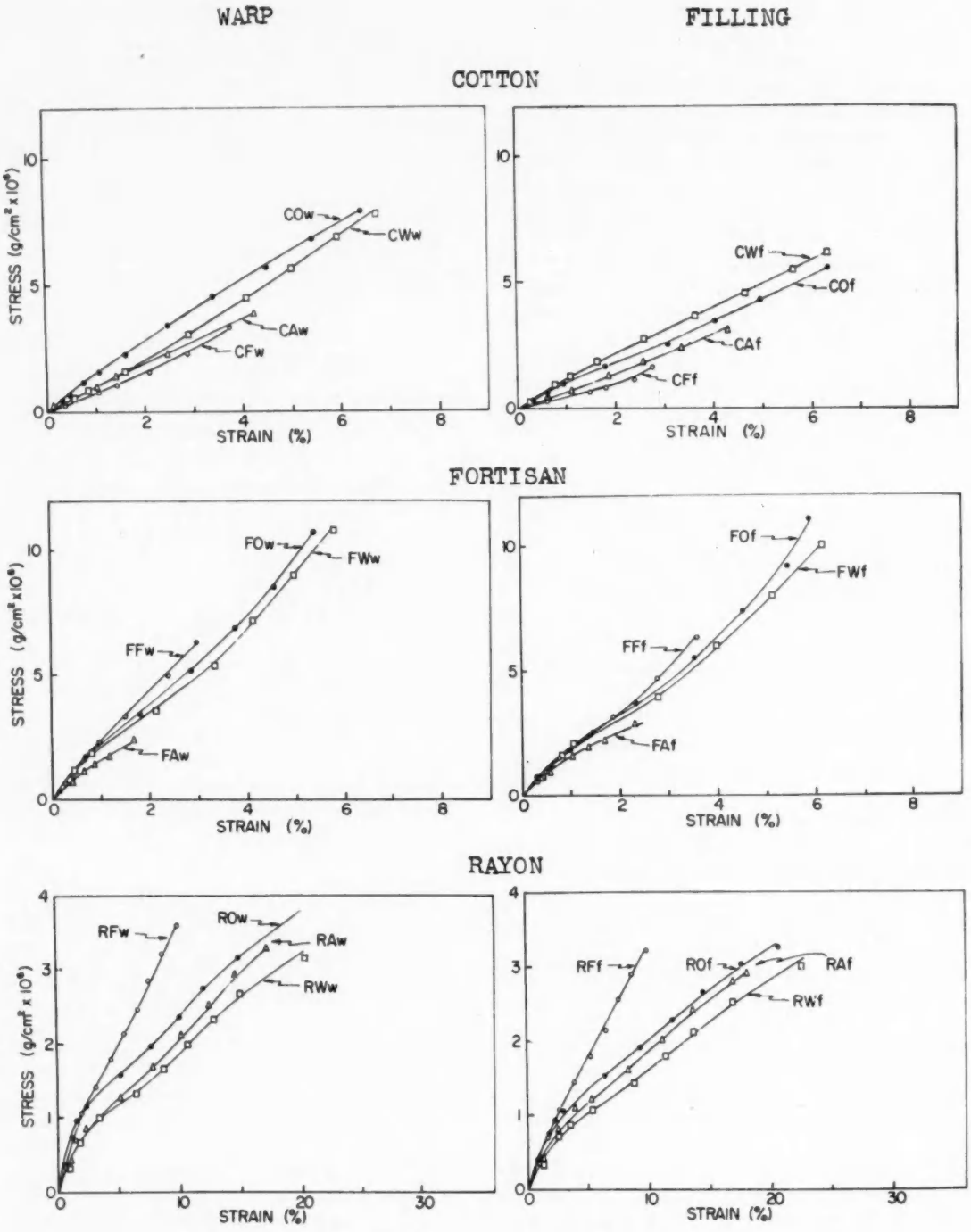


**Fig. 1.** Typical stress-strain curves for single fibers.

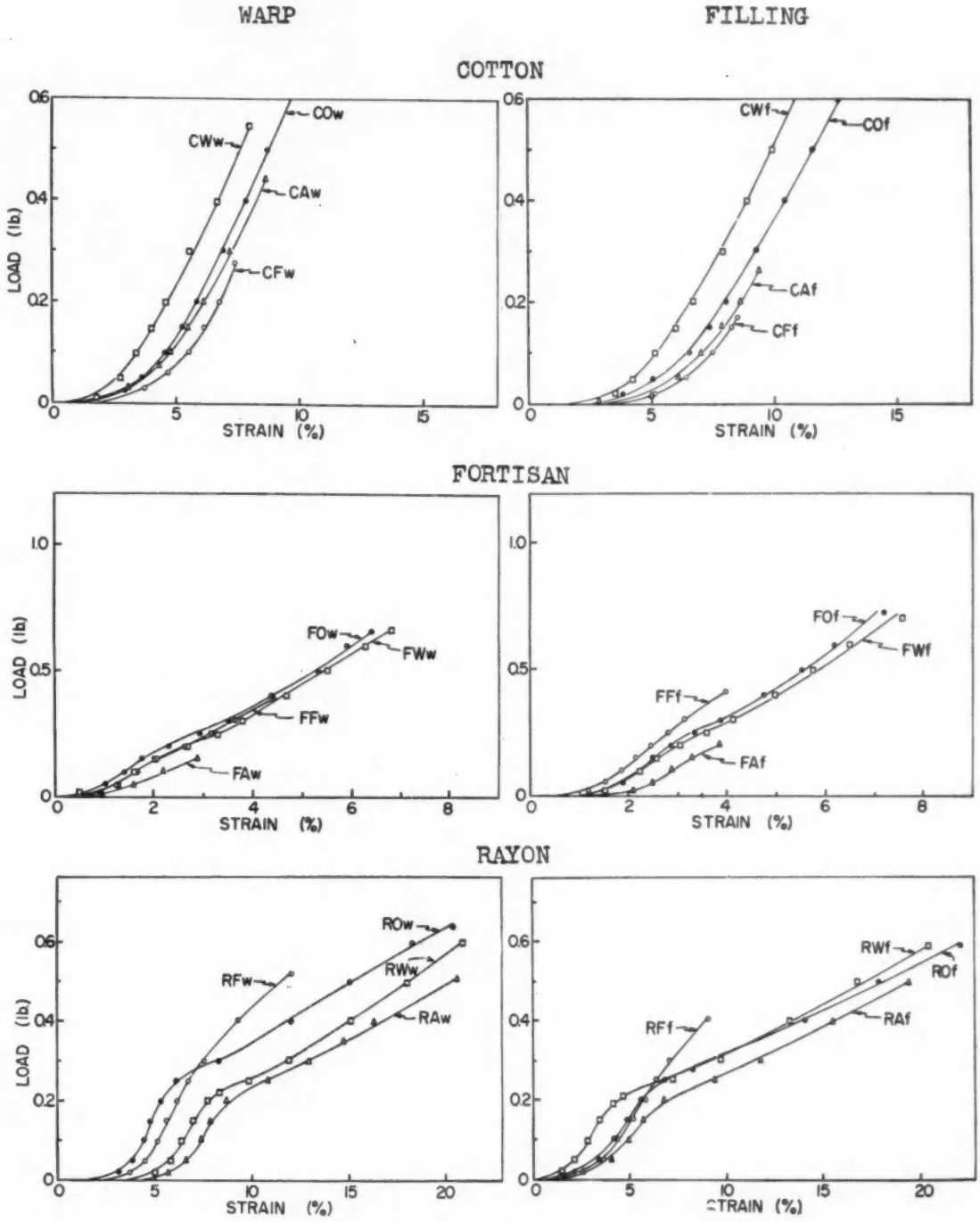


Fig. 2. Typical load-strain curves for yarns.

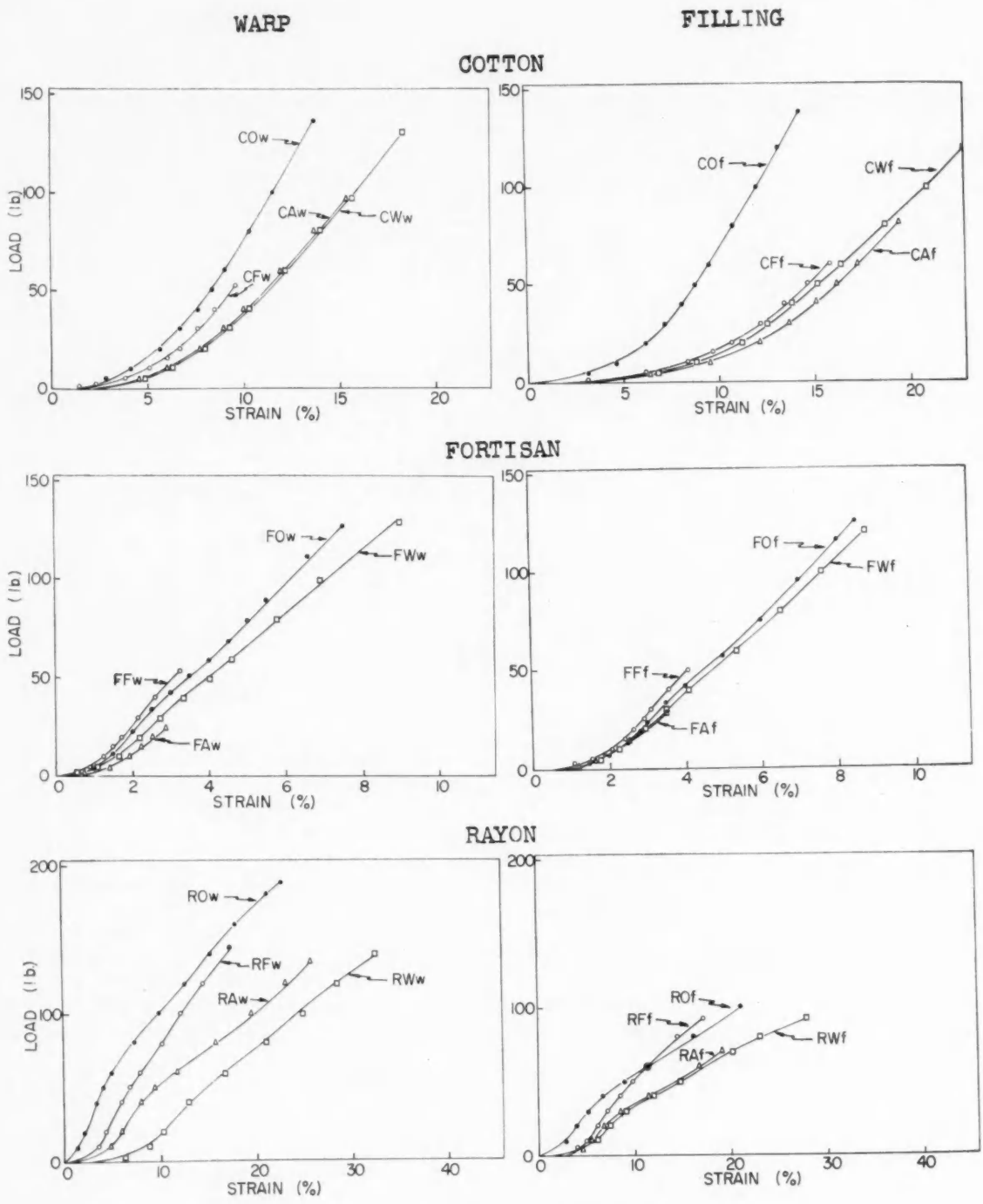


**Fig. 3.** Typical one-dimensional load-strain curves for fabrics.

cellulose fibers. Comparing the stress-strain behavior of the formaldehyde-treated samples with the corresponding acid-treated ones, it is interesting to note that cotton differs from rayon and Fortisan in that the formaldehyde-treated cotton is weaker in tensile strength, lower in elongation, and shows a lower elastic modulus than the "acid-control," while formaldehyde-treated Fortisan and rayon both show increases in strength and elastic modulus over their respective "acid-controls." The relative increase is greater in the case of Fortisan which also shows a substantial gain in elongation. The formaldehyde-treated rayon gives a stress-strain curve which is markedly different from those of the other treated rayon samples because of the absence of a prominent yield point.

Now it has long been known that the dry strength of native cellulose is lower than its wet strength, while the reverse is true in the case of regenerated cellulose fibers. Hermans [10] offered an explanation for this phenomenon in which he depicted the molecular chains of wet native cellulose fibers as strands of cords of more or less equal lengths. The regenerated cellulose fibers, having a higher proportion of amorphous regions, were compared to strands of cords of unequal lengths, some fairly straight and others kinked. In dry fibers, the intermolecular forces were likened to knotting the strands together. Imagine clamping these strands of cords in a rending machine; it is easy to see that $n$ strands of cords of similar lengths (wet native cellulose) will have a tensile strength of $n$ times the tensile strength of one cord. Knotting them together (dry native cellulose) results in a less even distribution of stress and, consequently, a lower tensile strength. On the other hand, in the case of $n$ cords of unequal length (wet regenerated cellulose) the tensile strength corresponds only to the strength of the shortest cord

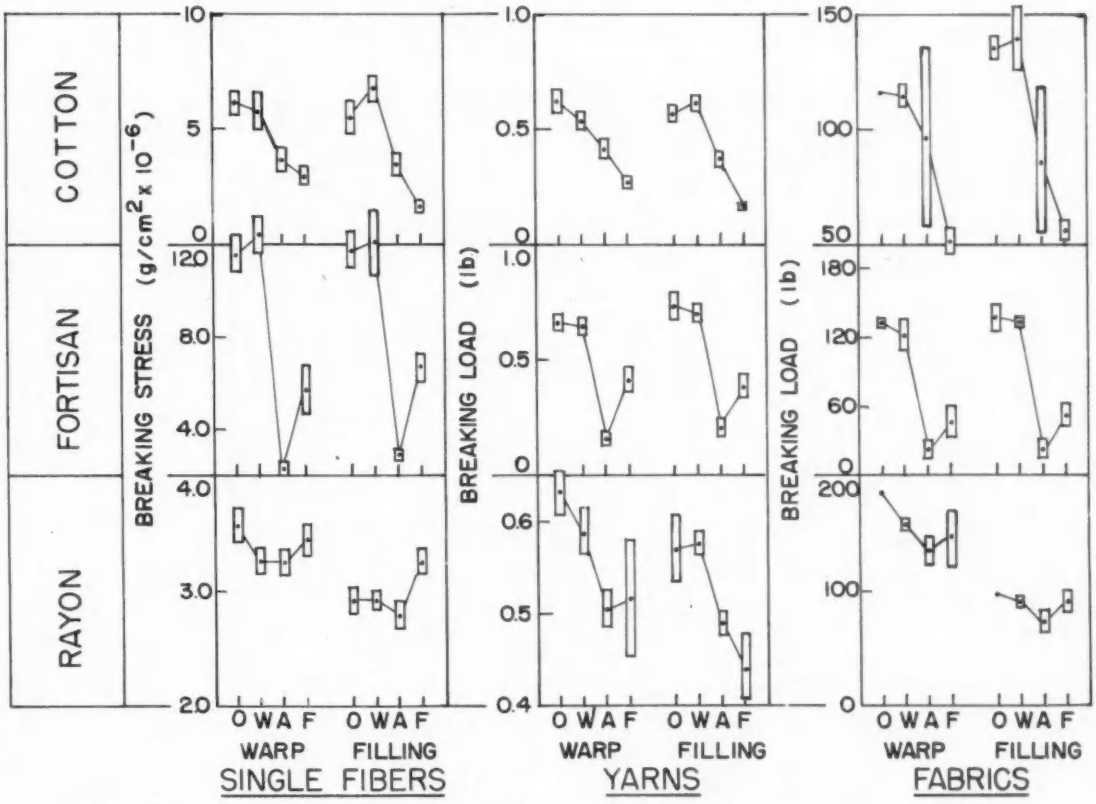


**Fig. 4.** Breaking stress or load vs. treatment. O = original untreated, W = water-treated, A = acid-treated, F = formaldehyde-treated.

between the clamps. Tying them together (dry regenerated cellulose) certainly will give a higher tensile strength. The results observed with the formaldehyde treatment in this study—the decrease in tensile strength of cotton after formaldehyde treatment as compared with the "acid-control" and the increase in the case of viscose rayon and Fortisan—are in accord with the above representation. These observations, therefore, clearly demonstrate that the formaldehyde treatment must have achieved some cross-linking between the cellulose chains. The higher relative increase in strength of formaldehyde-treated Fortisan over the "acid-control" may be explained by the closeness of average approach of the highly oriented cellulose molecules which should increase the probability of cross-linking. The absence of a prominent yield point of the formaldehyde-treated rayon sample points definitely to the formation of a cross-linked three-dimensional network.

Typical load-strain curves for the yarns are given in Figure 2. Examination of the curves for cotton, Fortisan, and rayon yarn reveals a remarkable correlation with the corresponding results for single fibers discussed above. In the case of rayon yarns, however, the formaldehyde treatment appears to result in a reduction both in breaking load and extensibility, whereas in the case of the single fibers of viscose rayon yarn, only the extensibility was reduced.

Typical load-strain curves obtained in one-dimensional tests of the fabrics are given in Figure 3. It is to be noted that here the untreated samples are markedly stiffer than all the other samples except for the formaldehyde-treated samples in some cases, which of course attain a higher stiffness due to cross-bonding effected in the molecular structure of the fiber. The untreated samples are fabrics as produced with conventional finishing equipment. The

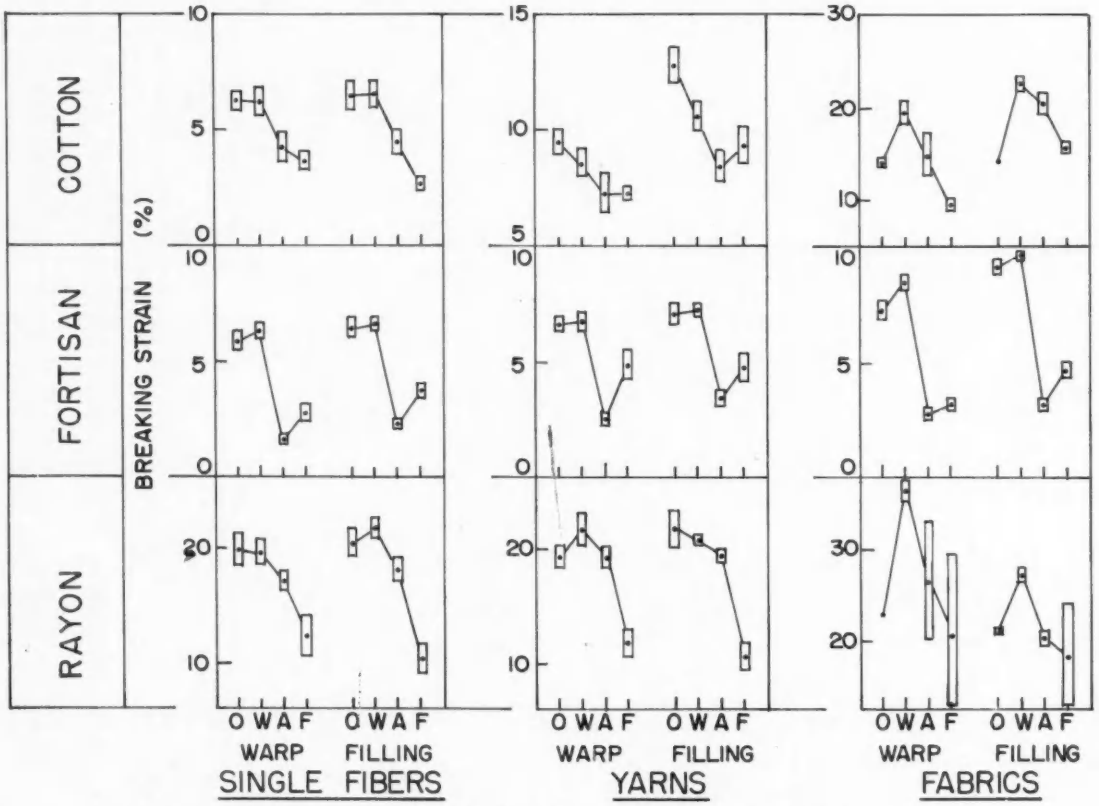


**Fig. 5.** Breaking strain vs. treatment. O = original untreated, W = water-treated, A = acid-treated, F = formaldehyde-treated.

tension sustained by the fabrics during the finishing operations generally results in a considerable amount of permanent deformation. Upon treating with water and baking, swelling recovery takes place, and the permanent deformation is removed. The untreated samples, therefore, depending on the tension in finishing, have a varying lesser amount of the plastic component of the fiber to start with, as compared to the treated samples. The difference is also observed to a lesser extent in yarns and fibers. In fabrics, the complicated geometry of the structure exaggerates the difference. This illustrates why the untreated sample is a very poor reference to use for the purpose of detecting effects resulting from changes in the molecular structure of the fiber.

The general effect of the acid treatment and the formaldehyde reaction, in relation to the water-treated control, is quite similar to that found for the yarn and single-fiber tests.

It should be emphasized that all of the stress-strain curves discussed in this section are "typical curves." It is not possible to present average stress-strain curves which have precise quantitative meaning. Hence, several significant tensile properties were derived from these curves, and the average values are discussed in the next section.

### 2. *Tensile Properties versus Treatments*

The number of specimens tested to give the mean values and confidence limits discussed later is listed for each fiber type in Table II.

The following tensile properties were derived from the stress- and load-strain curves: breaking stress or load, breaking elongation, elastic modulus, and toughness. These results are plotted in the form of charts in Figures 4–7. It should be noted that the vertical dimensions of the rectangles surrounding the plotted

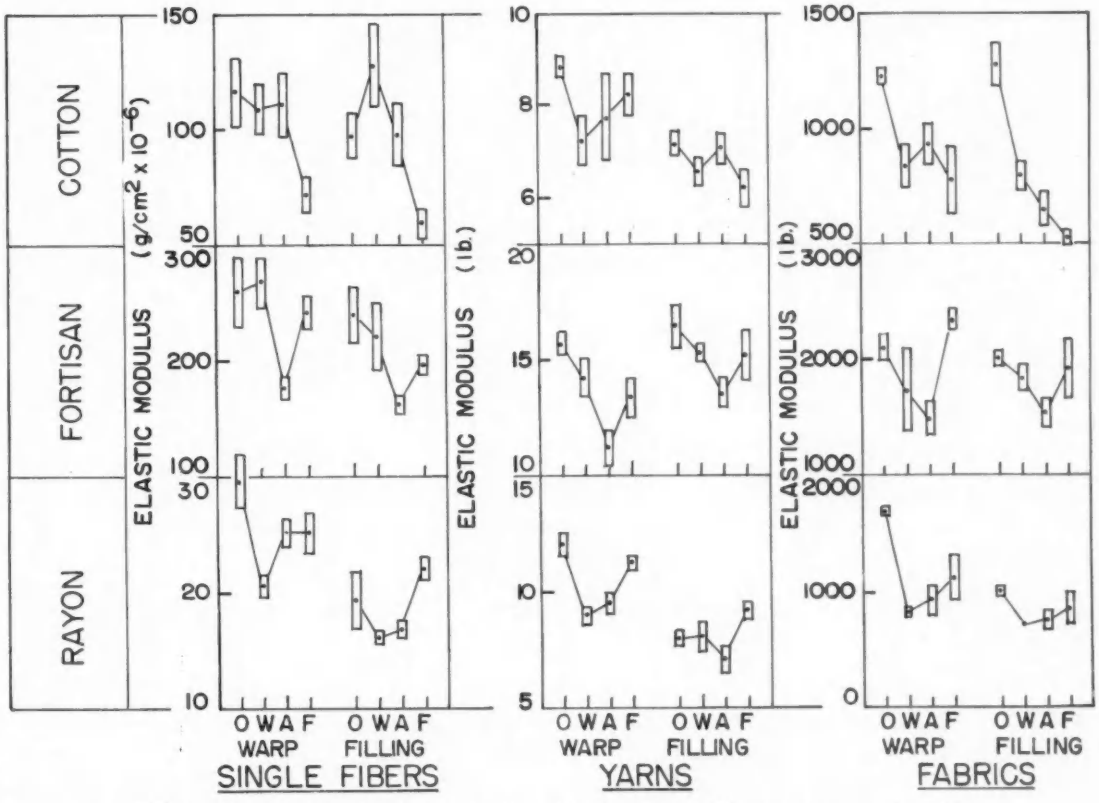


**Fig. 6.** Elastic modulus vs. treatment. O = original untreated, W = water-treated, A = acid-treated, F = formaldehyde-treated.

points represent 95% confidence limits of the corresponding mean values.

Scanning these four figures, it is remarkable to find such excellent correlation among the fiber, yarn, and fabric results for a given property and a given fiber. This correlation is particularly good in the case of Fortisan which lends encouragement as regards the significance of single-fiber measurements in relation to yarn and fabric performance.

**TABLE II. Summary of Numbers of Specimens Tested for Mechanical Behavior**

| Tests performed on | Number of specimens tested for each weave direction and treatment | | |
|---|---|---|---|
| | Cotton | Fortisan | Rayon |
| Single fibers | 25 | 15 | 15 |
| Yarns | 15 | 10 | 5 |
| Fabrics (one-dimensional) | 4 | 4 | 4 |
| Fabrics (two-dimensional) | 5 | 4* | 5* |

* In some instances, at higher extensions, measurements were made on two or three specimens.

The results on breaking stress or load, given in Figure 4, are consistent with the conclusions drawn from the typical stress- and load-strain curves discussed in the previous section. However, it must be noted that these results are true averages and thus the conclusions drawn from them are more significant than those derived from the curves.

The breaking elongation data of Figure 5 likewise yield no new conclusions which could not be drawn from the typical curves. This is not true in the case of the charts giving elastic modulus (Figure 6) and toughness (Figure 7). The elastic modulus data of Figure 6 are particularly interesting since they establish that the formaldehyde treatment decreases the modulus of cotton, whereas it tends to increase it

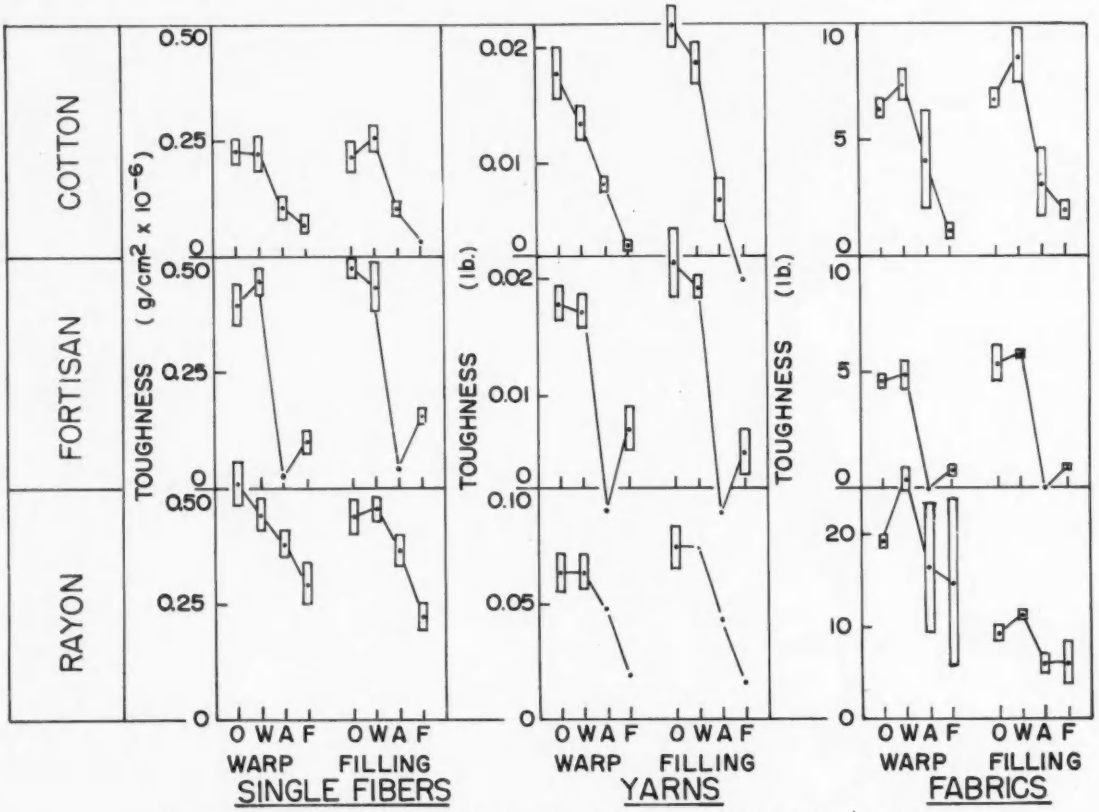


**Fig. 7.** Toughness vs. treatment. O = original untreated, W = water-treated, A = acid-treated, F = formaldehyde-treated.

markedly over that of the acid-treated samples in the case of the two regenerated cellulose fibers, Fortisan and rayon. In some cases, however, the elastic modulus has not been increased by formaldehyde treatment over that of the original and water-treated samples. In the case of cotton, this finding, that formaldehyde treatment lowers the elastic modulus, is unexpected and does not appear to have been noted previously in the literature. It is probably associated with the greater crystallinity of cotton, as compared to either Fortisan or rayon, but in view of the present experimental evidence, no speculations regarding the mechanism by which formaldehyde lowers the elastic modulus of cotton will be made at this time. The toughness plots of Figure 7 are unusually informative. Toughness is defined here as the area under the stress-strain curve to rupture and thus represents the energy to break. It is seen in the plots of Figure 7 that formaldehyde treatment greatly reduces the toughness of all three types of cellulose, in single-fiber, yarn, or fabric form. Hence, the cross-linking achieved by this particular type of formaldehyde treatment appears to produce unfavorable results, if high energy to break is desired. Only in the case of Fortisan does the treatment result in a slight increase in toughness in respect to the highly degraded acid control.

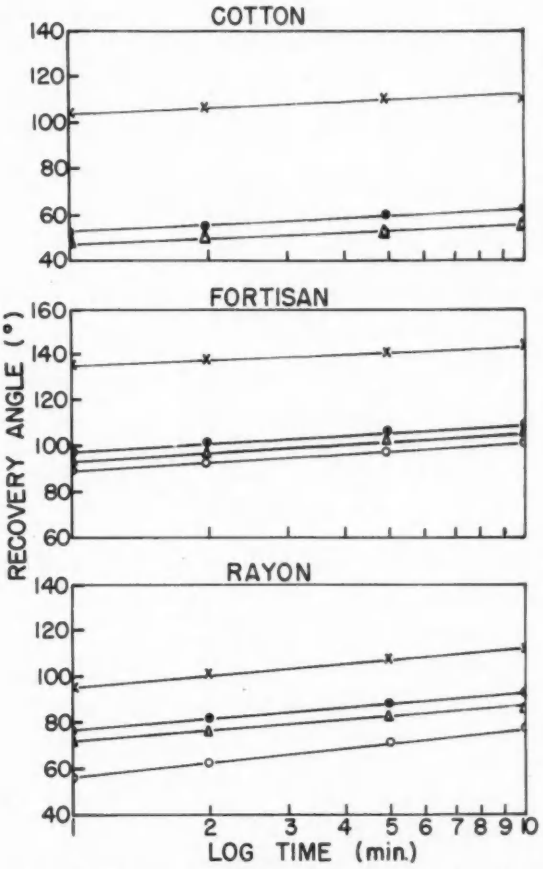


**Fig. 8.** Monsanto wrinkle recovery angle vs. log time. ● = original untreated, ○ = water treated, △ = acid treated, × = formaldehyde treated.

### *3. Wrinkle Recovery*

The Monsanto Wrinkle Recovery Angle is plotted against the logarithm of time in Figure 8 [5]. The values are the means of five tests each of the warp and the filling. From the results it is easily seen that with all the three fabrics, the formaldehyde-treated samples are distinguished by markedly greater wrinkle recovery angles than those of the controls. The relative increase is greatest in cotton, next in Fortisan, and lowest in rayon. When it is recalled that cotton is more highly crystalline than either of the two regenerated fibers, and thus has a smaller amorphous area where most cross-linking occurs, the large increase in recovery angle is not surprising. The greater increase in wrinkle recovery observed for Fortisan as compared to viscose rayon may possibly result from the greater bound formaldehyde observed in the case of Fortisan. The higher degree of orientation of the molecules in Fortisan also appears to favor cross-linking.

### *4. One-dimensional versus Two-dimensional Fabric Properties*

The conventional one-dimensional fabric tensile tests commonly employed in textile testing laboratories have been devised mainly on the basis of simplicity. Many workers have recognized that the test results obtained in this manner often are misleading since the stresses on fabrics in service are almost always two-dimensional. In actual service, stresses occur in both the warp and filling directions, and hence, the interaction of the two orthogonal sets of yarns, each set under simultaneous although often not equal loading, may be very important. It was upon this premise that the Textile Research Institute's two-dimensional testing device was developed. Previous data obtained with it [15, 20] have clearly indicated that the results of two-dimensional tests often

yield quite different results from those obtained by the conventional one-dimensional method. The curves of Figures 9–11 further demonstrate this point. The two-dimensional curves shown in these figures are composite curves constructed by averaging the elongation values corresponding to the same load levels of the individual tests and plotting these average values against the respective loads. From these curves certain strain levels are taken and the loads carried by the warp and the filling are determined. These ratios are converted into Asymmetry Indices [20] and plotted against two-dimensional strains, as shown in Figure 12.

It is to be noted that in the case of cotton and Fortisan, the degradation suffered by the acid control and the formaldehyde-treated sample is so great that the two-dimensional strain is extremely low. Consequently, the accuracy of the Asymmetry Index vs. two-dimensional strain plot is greatly reduced, owing to the fact that at low strains the interferences from such sources as unequal tension in the two directions of the specimen during mounting and other factors of fabric geometry could easily disturb the correct relative position of the curves of the warp-wise and the filling-wise test. While not much information is gained from these tests, they demonstrate, nevertheless, that the formaldehyde treatment on cotton and Fortisan under these particular conditions is so damaging that the fabric cannot function satisfactorily under "cross-straining." The one-dimensional test yields the same information about the damage by the toughness measurements. However, the information is on the warp and filling separately, each being measured independently of the other.

In the case of rayon, however, the curves of Figure 12c clearly indicate that the formaldehyde-treated sample has a higher Asymmetry Index than both the water-treated and the untreated samples. The acid-treated sample displays a very low Asymmetry Index, rising slowly and approaching the water-treated sample at the break. These results are consistent with the finding of a previous study [20], in which it was demonstrated that, with fabrics of the

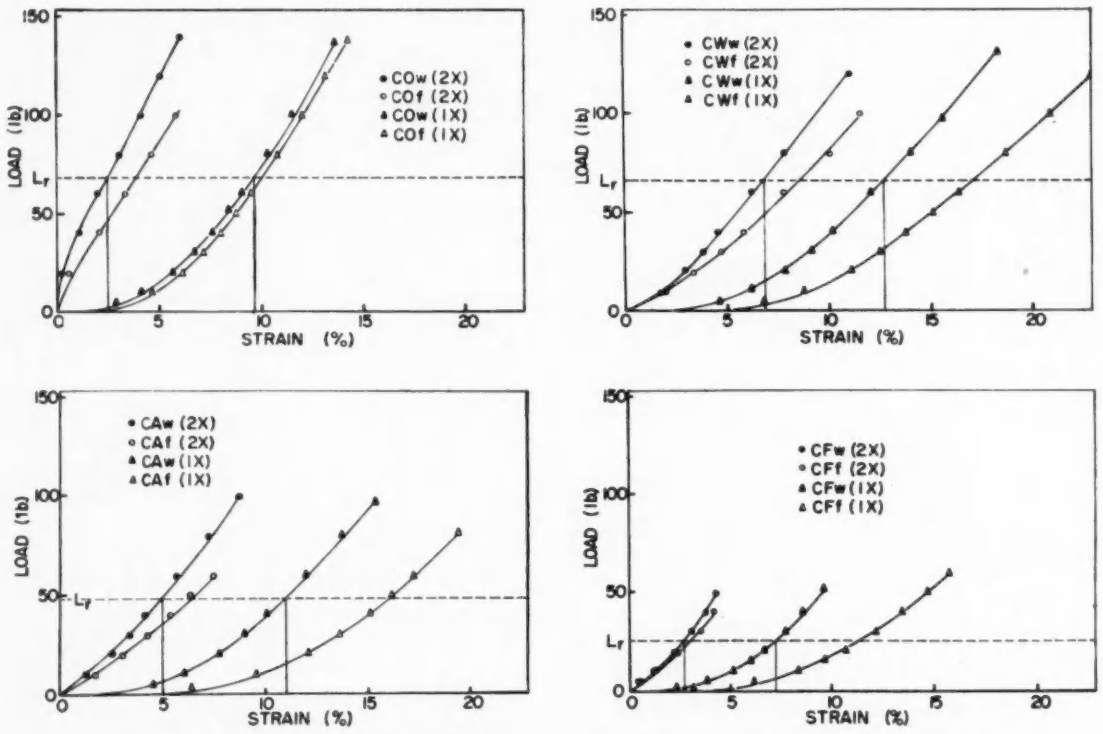


**Fig. 9.** Typical one-dimensional (1X); and two-dimensional (2X) load-strain curves for cotton fabrics.

same construction, cotton has a higher Asymmetry Index than nylon or Dacron. The interchain cohesion in the molecular network of cotton is believed to be stronger than that which exists in nylon or Dacron. With this set of rayon fabrics the formaldehyde-treated sample has the highest Asymmetry Index, presumably due to the increased interchain cohesion produced by cross-linking. The acid-treated sample has the lowest Asymmetry Index apparently due to the degradative action that cuts loose the interchain bonds.

The Asymmetry Index described above represents a measure of the ratio of loads sustained by the two orthogonal sets of yarns in a fabric while it is being extended in the two mutually perpendicular directions. The Asymmetry Index vs. two-dimensional strain plot gives a dynamic picture of the load-bearing ratio in the fabric under cross-straining. A similar treatment applied to the load-strain curves obtained will not have much significance, since these curves, as pointed out before, are obtained by straining the warp and the filling one-dimensionally independently of each other. In an effort to devise a quantitative index for comparison of the one- and two-dimensional load-elongation results, a strictly arbitrary quantity, labelled the "Asymmetry Energy Ratio," has been defined. Referring to the idealized curves of Figure 13, the Asymmetry Energy Ratio is defined as the difference in the energies to extend the warp and filling to an extension which corresponds to a load $L_r$ (arbitrarily selected as 50% of the breaking load of the warp in one-dimensional testing) divided by the energy to extend the warp to this load. In terms of the idealized curves as shown, the Asymmetry Energy Ratio, $E_2$, for the two-dimensional test is given by

$$E_2 = \frac{\text{Area } OAC - \text{Area } OBC}{\text{Area } OAC} = \frac{\text{Area } OAB}{\text{Area } OAC}$$

while the Asymmetry Energy Ratio, $E_1$, for one-dimensional testing is given by

$$E_1 = \frac{\text{Area } OA'C' - \text{Area } OB'C'}{\text{Area } OA'C'} = \frac{\text{Area } OA'B'}{\text{Area } OA'C'}$$

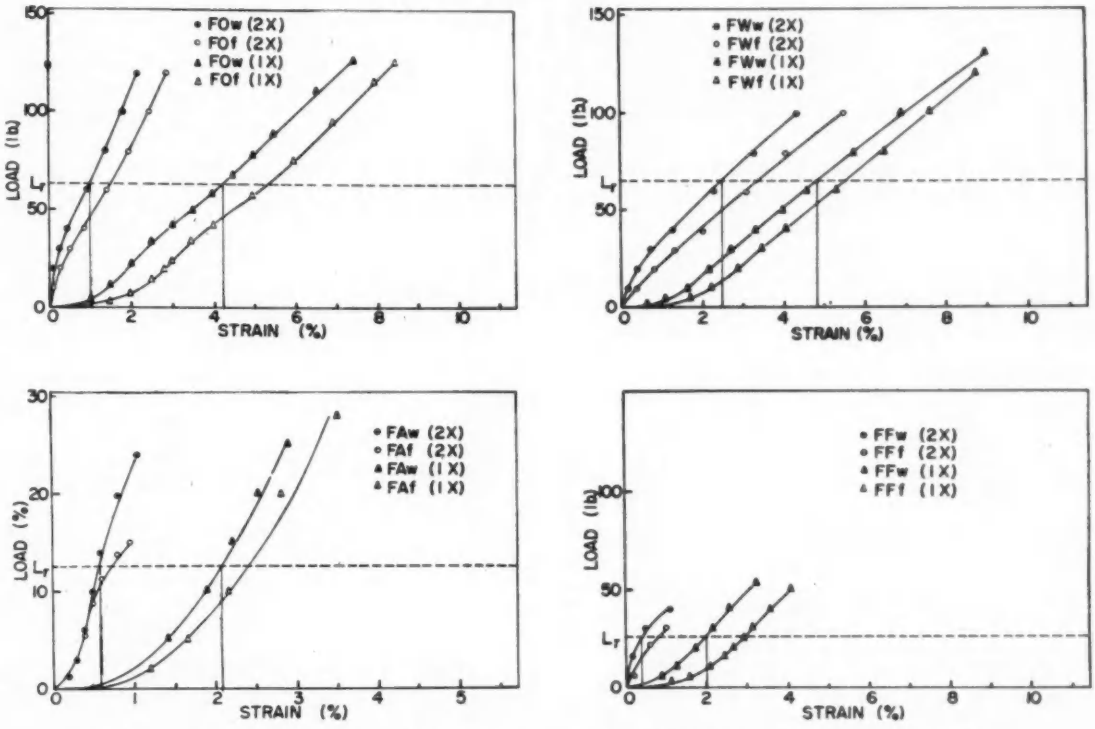


Fig. 10. Typical one-dimensional (1X); and two-dimensional (2X) load-strain curves for Fortisan fabrics.

Clearly this whole definition is quite arbitrary, although the employment of quantities with dimensions of energy to describe the load-elongation curves appears to be sound. In any event, this arbitrarily defined Asymmetry Energy Ratio seems to be worthy of tentative consideration and use.

*5. Comparison of Various Fabric Properties*

In Figure 14, the Asymmetry Energy Ratio, as defined in the previous section, is compared against fabric toughness and crease-recovery angle for the variously treated fabrics of cotton, Fortisan, and rayon. It is immediately apparent that fabric toughness proceeds with treatment almost in mirror-image fashion compared to crease-recovery angle, indicating the complete absence of a positive correlation of toughness with wrinkle recoverability. This result, as well as the results of other mechanical property measurements, suggests that cross-linking is solely responsible, in this instance, for imparting improved wrinkle recoverability to cellulosic fabrics. As has already been mentioned, the cross-linking operation probably reduces the irreversible slippage of cellulose chains past one another during fiber extension, thereby increasing elastic recovery from deformation and the crease recovery of fabrics made from the fibers [2, 5, 6, 7, 8, 9, 12].

The Asymmetry Energy Ratio appears to have very little relation to fabric toughness (there is really no reason why these two quantities should be related), but for the Fortisan and rayon fabrics, there is a striking correlation between the Asymmetry Energy Ratio and wrinkle-recovery angle. This is not true at all for the cotton fabric. It would seem that many more experiments must be performed before a fundamental basis can be developed for these correlations, but the results do suggest the possibility of obtaining very important information on fabric performance from measurements of this type analyzed in this manner.

## Conclusions

1. The screening tests of tensile strength and wrinkle recovery on all the formaldehyde-treated fabrics

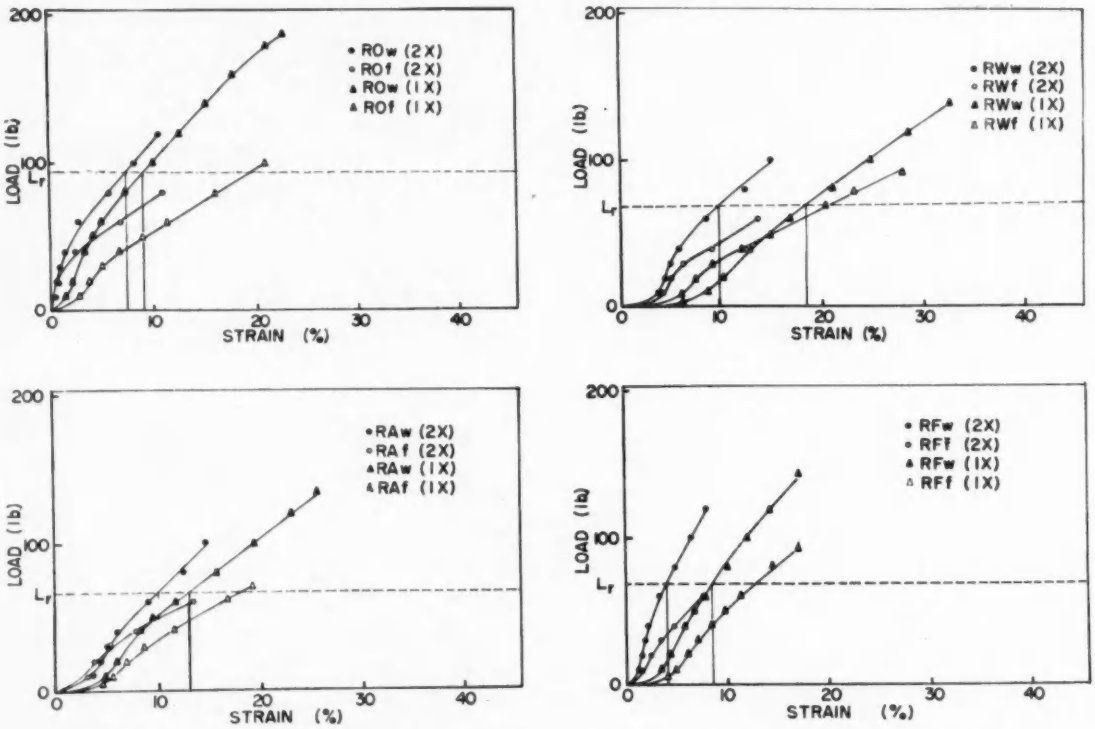


**Fig. 11.** Typical one-dimensional (1X); and two-dimensional (2X) load-strain curves for rayon fabrics.

resulting from the rate studies show that marked improvement in wrinkle recovery is obtained only with the fabrics treated at initial pH 2.0. From the rate and mechanism studies [19], it is found that at this pH, cross-linking in the amorphous regions is most extensive. This implies, therefore, that a high degree of cross-linking in the amorphous regions is necessary for an increase in wrinkle recoverability.

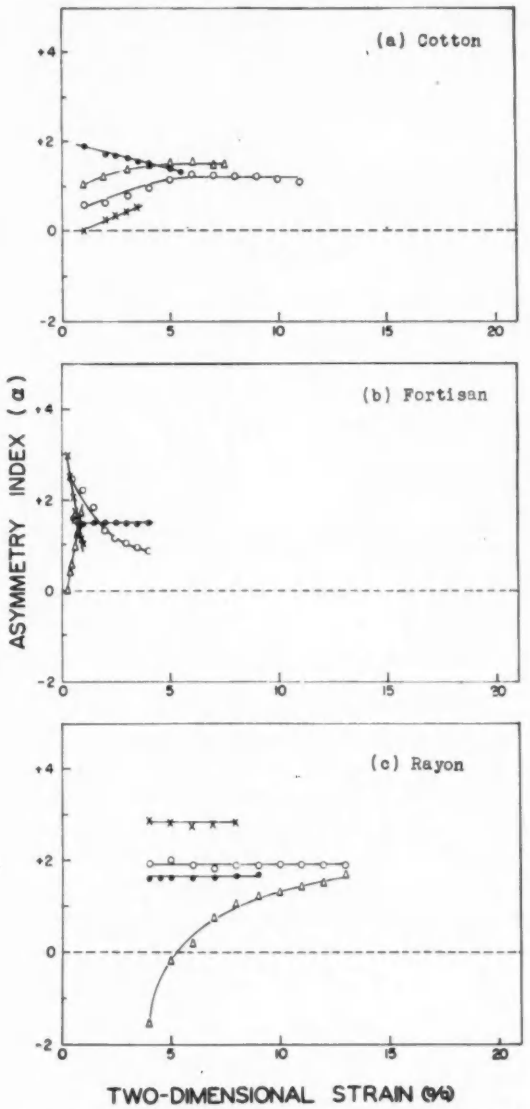


**Fig. 12.** Asymmetry Index vs. two-dimensional strain. ● = original untreated, ○ = water treated, △ = acid treated, × = formaldehyde treated.

Further studies on fabrics treated under optimum conditions reveal that wrinkle recoverability cannot be positively correlated with any of the tensile properties measured in this study.

2. Comparative studies of the fiber properties of the formaldehyde-treated samples under the optimum conditions and those of the "controls" indicate that the loss in tensile strength occurs mainly as a result of the inevitable acid hydrolytic degradation that accompanies the formaldehyde treatment. The stiffening of the molecular network resulting from cross-linking, however, could also be partly responsible for losses in extensibility and toughness. The fact that cotton loses still more strength with formaldehyde treatment while rayon and Fortisan show a gain over the acid control is seen as an expected result of cross-linking celluloses of different states of internal order.

3. From the two-dimensional tests of the fabrics, it is found that the formaldehyde treatment, as applied under the optimum conditions in this study, is highly detrimental to cotton and Fortisan. Formaldehyde-treated viscose rayon shows a higher Asymmetry Index at all two-dimensional strain levels as compared to the controls. The result is consistent with the finding of the previous work on two-dimensional testing with different fibers in fabrics of similar geometry. It indicates that the formaldehyde treatment has increased the interchain cohesive forces in the molecular network of the fiber.

4. An Asymmetry Energy Ratio is introduced in an effort to compare the results of one-dimensional and two-dimensional testing of fabric properties on a quantitative basis. A positive correlation between wrinkle recovery and Asymmetry Energy Ratio in

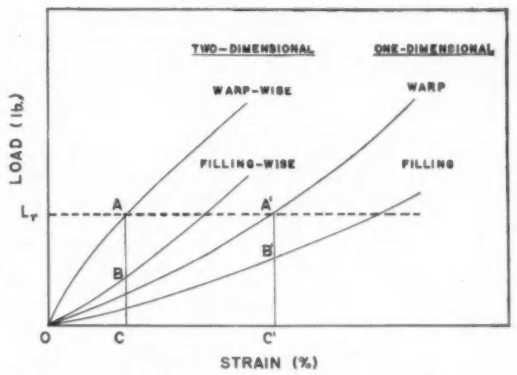


**Fig. 13.** Idealized load-strain curves of one-dimensional and two-dimensional fabric tests.

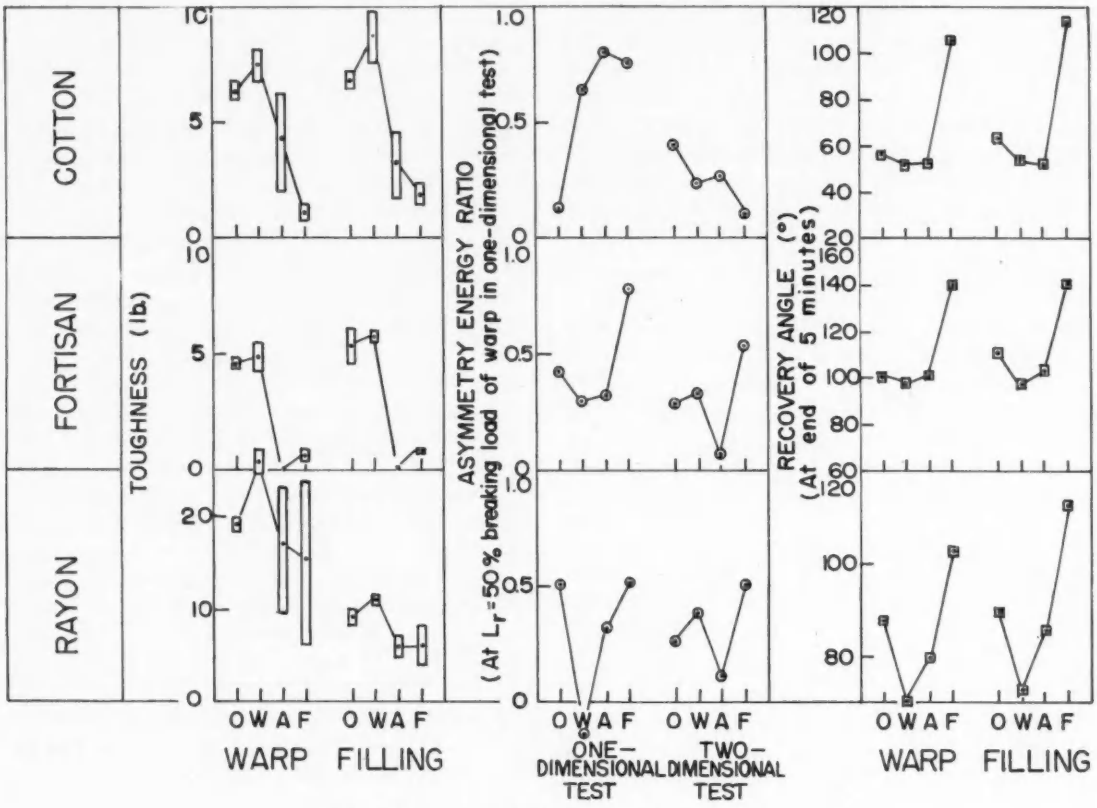


**Fig. 14.** Comparison of fabric properties vs. treatment.

the cases of Fortisan and rayon is indicated. Further studies are, however, necessary to establish the usefulness of this arbitrarily defined quantity.

5. In yarns and fabrics (one-dimensional testing), inherent fiber properties still predominate; i.e., the same differences and similarities observed in fiber properties persist in most instances in yarn and fabric behavior.

### Acknowledgments

This work was carried out as a part of Textile Research Institute's General Research Program. One of the authors, H. K. Woo, thanks the Goodyear Tire and Rubber Company for its fellowship grant in support of this research. Thanks are due Professor J. C. Whitwell for his advice regarding the statistical aspects of the work and E. Crystal for his assistance in some of the statistical calculations. The assistance of G. D. Mallory of the Goodyear Tire and Rubber Company in supplying the cotton and Fortisan fabric samples is gratefully acknowledged. The viscose rayon fabric was kindly supplied by J. A. Woodruff of the American Viscose Corporation.

# Appendix

**TABLE III. Breaking Strength and Elongation of Cotton Fabrics**
(Warp direction)

| Treatment conditions | | | Treatment time in minutes | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 5 | | 10 | | 15 | | 30 | |
| | | | Breaking strength in lb. and elongation in % | | | | | | | |
| pH | HCHO% | °C. | lb. | % | lb. | % | lb. | % | lb. | % |
| 2.0 | 5.0 | 110 | 78.7 | 11.7 | 73.0 | 11.1 | 94.5 | 12.4 | 60.1 | 9.6 |
| | | 120 | 70.9 | 10.9 | 71.5 | 10.6 | 63.0 | 9.7 | 62.7 | 9.8 |
| | | 130 | 78.4 | 10.2 | 67.8 | 10.3 | 44.1 | 8.8 | 58.2 | 9.8 |
| | 7.5 | 110 | 53.0 | 9.0 | 72.6 | 10.9 | 75.3 | 10.3 | 42.7 | 8.4 |
| | | 120 | 54.6 | 9.8 | 53.7 | 9.1 | 53.7 | 9.2 | 42.4 | 8.0 |
| | | 130 | 59.4 | 9.5 | 48.3 | 9.0 | 50.7 | 9.2 | 47.5 | 8.5 |
| | 10.0 | 110 | 67.9 | 10.8 | 50.0 | 9.0 | 56.9 | 9.2 | 50.6 | 8.9 |
| | | 120 | 49.0 | 8.9 | 51.4 | 9.1 | 63.0 | 9.9 | 42.0 | 8.3 |
| | | 130 | 43.4 | 8.4 | 55.2 | 9.5 | 64.2 | 9.3 | 57.1 | 8.2 |
| 2.2 | 5.0 | 110 | 143.6 | 19.2 | 148.0 | 18.4 | 132.6 | 17.1 | 132.2 | 16.6 |
| | | 120 | 128.5 | 18.4 | 125.8 | 18.8 | 100.0 | 15.0 | 98.2 | 15.5 |
| | | 130 | 121.8 | 18.0 | 103.8 | 15.5 | 103.1 | 15.3 | 76.9 | 12.6 |
| | 7.5 | 110 | 140.0 | 19.1 | 139.9 | 17.4 | 130.0 | 17.0 | 122.6 | 14.6 |
| | | 120 | 131.0 | 18.8 | 121.2 | 18.2 | 100.0 | 15.3 | 101.0 | 15.3 |
| | | 130 | 114.0 | 17.8 | 94.0 | 14.5 | 100.0 | 15.6 | 91.4 | 14.2 |
| | 10.0 | 110 | 145.0 | 18.1 | 127.2 | 16.6 | 138.1 | 17.8 | 124.8 | 16.0 |
| | | 120 | 123.0 | 17.8 | 125.3 | 17.7 | 109.8 | 15.4 | 106.4 | 15.5 |
| | | 130 | 105.7 | 16.7 | 85.3 | 14.6 | 93.0 | 14.7 | 75.5 | 13.6 |
| 2.4 | 5.0 | 110 | 149.0 | 18.0 | 142.2 | 16.9 | 145.8 | 16.7 | 121.2 | 15.3 |
| | | 120 | 122.8 | 18.3 | 119.2 | 16.9 | 115.6 | 16.4 | 111.4 | 16.3 |
| | | 130 | 133.1 | 18.5 | 117.6 | 17.3 | 109.3 | 15.6 | 98.2 | 15.0 |
| | 7.5 | 110 | 148.5 | 18.6 | 137.5 | 17.9 | 145.2 | 18.5 | 126.6 | 15.9 |
| | | 120 | 128.8 | 18.1 | 123.8 | 17.5 | 117.2 | 16.6 | 112.1 | 16.1 |
| | | 130 | 125.3 | 17.8 | 105.0 | 16.5 | 109.5 | 16.2 | 79.4 | 14.3 |
| | 10.0 | 110 | 151.3 | 18.3 | 142.8 | 17.3 | 144.5 | 17.4 | 136.9 | 17.1 |
| | | 120 | 138.0 | 17.7 | 119.0 | 17.1 | 121.1 | 16.9 | 115.5 | 17.6 |
| | | 130 | 126.1 | 17.5 | 110.4 | 16.2 | 100.0 | 14.9 | 99.7 | 14.8 |
| | Untreated | | 133.3 | 14.0 | (Average of 5 tests) | | | | | |

**TABLE IV. Breaking Strength and Elongation of Fortisan Fabrics**

(Warp direction)

| Treatment conditions | | | Treatment time in minutes | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 5 | | 10 | | 15 | | 30 | |
| | | | Breaking strength in lb. and elongation in % | | | | | | | |
| pH | HCHO% | °C. | lb. | % | lb. | % | lb. | % | lb. | % |
| 2.0 | 2.5 | 110 | 73.3 | 5.40 | 67.7 | 4.67 | 69.3 | 4.85 | 57.4 | 4.30 |
| | | 120 | 53.5 | 3.91 | 51.6 | 3.91 | 58.2 | 4.54 | 55.0 | 4.27 |
| | | 130 | 47.8 | 3.85 | 49.3 | 3.94 | 50.2 | 3.66 | 54.3 | 4.45 |
| | 5.0 | 110 | 77.8 | 5.43 | 63.7 | 4.52 | 62.6 | 4.35 | 62.4 | 3.90 |
| | | 120 | 62.3 | 3.91 | 59.5 | 3.95 | 52.7 | 3.71 | 57.8 | 3.85 |
| | | 130 | 62.2 | 4.04 | 56.4 | 3.28 | 55.8 | 3.32 | 52.1 | 3.18 |
| | 7.5 | 110 | 81.0 | 4.54 | 64.0 | 3.63 | 60.2 | 3.41 | 60.5 | 3.47 |
| | | 120 | 70.2 | 4.39 | 58.2 | 3.62 | 53.1 | 3.13 | 57.6 | 3.17 |
| | | 130 | 59.3 | 3.86 | 53.9 | 3.44 | 45.0 | 2.52 | 50.0 | 3.21 |
| 2.2 | 2.5 | 110 | 115.0 | 7.40 | 109.1 | 7.17 | 111.8 | 7.10 | 108.0 | 7.03 |
| | | 120 | 113.0 | 7.10 | 110.5 | 7.12 | 112.0 | 7.36 | 111.2 | 6.99 |
| | | 130 | 107.9 | 6.88 | 113.6 | 7.12 | 104.5 | 6.90 | 97.1 | 6.24 |
| | 5.0 | 110 | 111.2 | 7.70 | 108.9 | 7.04 | 112.6 | 7.27 | 110.8 | 7.22 |
| | | 120 | 100.1 | 7.19 | 107.5 | 7.03 | 98.5 | 7.05 | 104.2 | 6.41 |
| | | 130 | 114.6 | 7.33 | 109.9 | 6.53 | 97.2 | 6.35 | 100.6 | 6.48 |
| | 7.5 | 110 | 119.2 | 7.76 | 115.5 | 7.41 | 108.8 | 7.40 | 101.7 | 6.75 |
| | | 120 | 114.6 | 7.37 | 111.7 | 7.24 | 102.7 | 7.04 | 107.7 | 6.98 |
| | | 130 | 113.8 | 7.49 | 102.6 | 6.83 | 101.2 | 6.86 | 96.8 | 6.12 |
| 2.4 | 2.5 | 110 | 116.6 | 7.23 | 109.5 | 7.35 | 107.0 | 7.32 | 118.2 | 7.61 |
| | | 120 | 112.1 | 7.44 | 113.1 | 7.38 | 100.3 | 7.25 | 109.4 | 7.02 |
| | | 130 | 112.8 | 7.48 | 104.6 | 7.00 | 105.3 | 6.95 | 108.4 | 6.75 |
| | 5.0 | 110 | 115.4 | 7.74 | 116.7 | 7.83 | 116.4 | 7.33 | 112.0 | 7.00 |
| | | 120 | 113.8 | 7.52 | 115.0 | 7.65 | 110.2 | 7.21 | 115.4 | 6.97 |
| | | 130 | 113.0 | 7.45 | 113.3 | 7.42 | 107.0 | 7.75 | 106.2 | 6.53 |
| | 7.5 | 110 | 119.1 | 8.16 | 114.0 | 7.60 | 114.0 | 7.65 | 115.3 | 7.62 |
| | | 120 | 113.9 | 7.69 | 110.1 | 7.21 | 112.7 | 7.28 | 111.0 | 7.35 |
| | | 130 | 106.0 | 7.34 | 113.5 | 7.61 | 101.4 | 6.80 | 101.8 | 7.36 |
| | Untreated | | 132.1 | 7.30 | (Average of 5 tests) | | | | | |

**TABLE V. Breaking Strength and Elongation of Rayon Fabrics**

(Warp direction)

| Treatment conditions | | | Treatment time in minutes | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 5 | | 10 | | 15 | | 30 | |
| | | | Breaking strength in lb. and elongation in % | | | | | | | |
| pH | HCHO% | °C. | lb. | % | lb. | % | lb. | % | lb. | % |
| 2.0 | 2.5 | 110 | 169.2 | 27.7 | 167.9 | 28.6 | 166.2 | 27.3 | 157.5 | 20.3 |
| | | 120 | 167.8 | 23.3 | 167.0 | 23.1 | 165.2 | 23.6 | 165.6 | 18.8 |
| | | 130 | 159.2 | 22.9 | 168.6 | 23.2 | 165.0 | 20.5 | 156.1 | 18.0 |
| | 5.0 | 110 | 160.0 | 25.4 | 170.9 | 27.4 | 158.3 | 21.4 | 157.5 | 17.1 |
| | | 120 | 159.5 | 20.0 | 159.1 | 20.5 | 153.6 | 18.3 | 150.9 | 16.1 |
| | | 130 | 154.4 | 18.7 | 159.9 | 21.0 | 154.9 | 19.2 | 163.5 | 16.3 |
| | 7.5 | 110 | 165.7 | 23.2 | 130.0 | 17.2 | 139.2 | 18.2 | 155.5 | 15.1 |
| | | 120 | 157.4 | 18.7 | 144.0 | 17.7 | 146.4 | 17.6 | 151.5 | 16.2 |
| | | 130 | 155.2 | 20.1 | 148.0 | 17.2 | 149.6 | 14.7 | 144.6 | 14.0 |
| 2.2 | 2.5 | 110 | 168.3 | 31.6 | 169.6 | 34.3 | 171.7 | 31.3 | 170.7 | 29.8 |
| | | 120 | 168.5 | 29.8 | 175.2 | 31.6 | 168.2 | 30.6 | 182.1 | 30.3 |
| | | 130 | 170.9 | 30.1 | 170.6 | 28.1 | 164.0 | 28.2 | 172.7 | 29.6 |
| | 5.0 | 110 | 173.8 | 31.5 | 176.0 | 31.7 | 173.8 | 30.5 | 174.0 | 30.9 |
| | | 120 | 186.7 | 30.9 | 184.6 | 31.3 | 187.6 | 28.9 | 178.2 | 28.1 |
| | | 130 | 166.6 | 28.5 | 181.4 | 28.0 | 156.5 | 27.1 | 176.0 | 27.9 |
| | 7.5 | 110 | 169.5 | 32.4 | 175.8 | 32.1 | 173.2 | 32.4 | 173.4 | 30.7 |
| | | 120 | 172.9 | 31.3 | 171.0 | 32.9 | 168.4 | 30.1 | 170.9 | 29.5 |
| | | 130 | 176.6 | 30.7 | 178.2 | 28.0 | 174.3 | 27.8 | 182.8 | 28.0 |
| 2.4 | 2.5 | 110 | 175.0 | 33.3 | 175.5 | 33.1 | 173.5 | 31.8 | 175.1 | 32.9 |
| | | 120 | 168.4 | 31.7 | 167.1 | 31.4 | 176.0 | 32.0 | 176.0 | 33.3 |
| | | 130 | 169.0 | 31.5 | 165.0 | 30.9 | 169.9 | 30.8 | 172.0 | 28.4 |
| | 5.0 | 110 | 172.9 | 32.6 | 162.2 | 31.4 | 176.3 | 31.0 | 170.0 | 32.0 |
| | | 120 | 168.3 | 32.9 | 167.8 | 30.3 | 176.9 | 31.9 | 178.9 | 29.3 |
| | | 130 | 166.5 | 30.8 | 168.5 | 28.5 | 167.4 | 29.4 | 170.0 | 29.4 |
| | 7.5 | 110 | 175.5 | 34.5 | 177.8 | 31.9 | 175.8 | 30.4 | 175.0 | 30.5 |
| | | 120 | 170.2 | 33.1 | 174.6 | 31.8 | 180.0 | 32.0 | 180.8 | 30.7 |
| | | 130 | 169.7 | 30.1 | 178.2 | 30.9 | 170.2 | 30.8 | 175.2 | 26.7 |
| | Untreated | | 187.0 | 22.9 | (Average of 5 tests) | | | | | |

**TABLE VI. Wrinkle Recovery of Fabrics**

(Warp direction)

| Treatment conditions | Wrinkle recovery angle (Reading taken after 5 min.) Treatment time in min. 5 | 10 | 15 | 30 |
|---|---|---|---|---|
| **COTTON** | | | | |
| pH 2.0 | | | | |
| HCHO 5.0%, 110° C. | 116° | 86° | 85° | 96°* |
| 120 | 110 | 121 | 90 | 96 |
| 130 | 107 | 93 | 109 | 96 |
| HCHO 7.5%, 110 | 100 | 77 | 88 | 109* |
| 120 | 110 | 100 | 129 | 119 |
| 130 | 117 | 116 | 120 | 121 |
| HCHO 10%, 110 | 110 | 95 | 100 | 123 |
| 120 | 97 | 107 | 130 | 120 |
| 130 | 107 | 120 | 97 | 125 |
| pH 2.2 | | | | |
| HCHO 5.0%, 110 | 57 | 57 | 59 | 58 |
| 120 | 70 | 72 | 85 | 88 |
| 130 | 90 | 87 | 96 | 90 |
| HCHO 7.5%, 110 | 50 | 52 | 64 | 61 |
| 120 | 77 | 65 | 73 | 68 |
| 130 | 68 | 63 | 77 | 109 |
| HCHO 10%, 110 | 46 | 50 | 48 | 64 |
| 120 | 61 | 74 | 74 | 99 |
| 130 | 79 | 80 | 79 | 102 |
| pH 2.4 | | | | |
| HCHO 5.0%, 110 | 36 | 55 | 50 | 52 |
| 120 | 74 | 68 | 65 | 70 |
| 130 | 75 | 82 | 71 | 87 |
| HCHO 7.5%, 110 | 51 | 56 | 47 | 58 |
| 120 | 54 | 49 | 70 | 92 |
| 130 | 67 | 62 | 85 | 79 |
| HCHO 10%, 110 | 52 | 50 | 51 | 62 |
| 120 | 68 | 68 | 71 | 72 |
| 130 | 70 | 62 | 77 | 80 |
| Original untreated sample | 73°* | | | |
| **FORTISAN** | | | | |
| pH 2.0 | | | | |
| HCHO 2.5%, 110° C. | 97° | 102° | 102° | 110° |
| 120 | 127 | 118 | 136 | 131 |
| 130 | 131 | 131 | 130 | 138 |
| HCHO 5.0%, 110 | 103 | 130 | 140 | 142* |
| 120 | 134 | 142 | 141 | 132 |
| 130 | 134 | 158 | 131 | 148 |
| HCHO 7.5%, 110 | 130 | 149 | 144 | 153* |
| 120 | 147 | 150 | 152 | 145 |
| 130 | 152 | 144 | 152 | 150 |
| pH 2.2 | | | | |
| HCHO 2.5%, 110 | 89 | 100 | 106 | 84 |
| 120 | 88 | 81 | 96 | 101 |
| 130 | 99 | 94 | 99 | 99 |
| HCHO 5.0%, 110 | 85 | 85 | 110 | 83 |
| 120 | 93 | 100 | 98 | 107 |
| 130 | 105 | 97 | 101 | 105 |

(Warp direction)

| Treatment conditions | Wrinkle recovery angle (Reading taken after 5 min.) Treatment time in min. 5 | 10 | 15 | 30 |
|---|---|---|---|---|
| **FORTISAN CONT'D.** | | | | |
| pH 2.2 | | | | |
| HCHO 7.5%, 110 | 98 | 98 | 96 | 104 |
| 120 | 89 | 80 | 90 | 90 |
| 130 | 90 | 106 | 102 | 107 |
| pH 2.4 | | | | |
| HCHO 2.5%, 110 | 105 | 99 | 88 | 105 |
| 120 | 85 | 89 | 91 | 99 |
| 130 | 80 | 92 | 98 | 87 |
| HCHO 5.0%, 110 | 81 | 72 | 91 | 101 |
| 120 | 102 | 76 | 77 | 100 |
| 130 | 90 | 94 | 87 | 94 |
| HCHO 7.5%, 110 | 102 | 90 | 93 | 99 |
| 120 | 103 | 82 | 90 | 107 |
| 130 | 100 | 99 | 99 | 101 |
| Original untreated sample | 110°* | | | |
| **RAYON** | | | | |
| pH 2.0 | | | | |
| HCHO 2.5%, 110° C. | 91° | 82° | 71° | 89° |
| 120 | 64 | 82 | 93 | 88 |
| 130 | 100 | 91 | 89 | 91 |
| 5.0%, 110 | 93 | 87 | 100 | 109* |
| 120 | 112 | 115 | 120 | 105 |
| 130 | 110 | 116 | 129 | 135 |
| 7.5%, 110 | 83 | 84 | 85 | 131* |
| 120 | 81 | 95 | 93 | 134 |
| 130 | 95 | 77 | 83 | 130 |
| pH 2.2 | | | | |
| HCHO 2.5%, 110 | 69 | 77 | 89 | 67 |
| 120 | 84 | 82 | 80 | 64 |
| 130 | 78 | 78 | 76 | 76 |
| HCHO 5.0%, 110 | 105 | 86 | 61 | 89 |
| 120 | 92 | 92 | 96 | 103 |
| 130 | 88 | 87 | 88 | 91 |
| HCHO 7.5%, 110 | 70 | 80 | 94 | 72 |
| 120 | 86 | 76 | 92 | 95 |
| 130 | 86 | 80 | 103 | 100 |
| pH 2.4 | | | | |
| HCHO 2.5%, 110 | 84 | 88 | 94 | 85 |
| 120 | 78 | 72 | 99 | 83 |
| 130 | 76 | 84 | 86 | 86 |
| HCHO 5.0%, 110 | 83 | 70 | 80 | 83 |
| 120 | 88 | 83 | 88 | 91 |
| 130 | 84 | 91 | 105 | 84 |
| HCHO 7.5%, 110 | 75 | 79 | 100 | 74 |
| 120 | 84 | 75 | 87 | 84 |
| 130 | 76 | 70 | 96 | 81 |
| Original untreated sample | 80°* | | | |

* Five measurements; others one measurement.

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# Studies on Water Repellency of Organic Silicon Compounds

## Part III: Water Resistance of Fabrics Treated with Methylpolysiloxane Containing Thiuronium Chloride[1]

**Kazumune Nakao,[2] Nobuaki Wada,[2] Kyozo Nakasima,[2] and Shunichi Nozakura[3]**

**Abstract**

A new water-soluble linear methylpolysiloxane containing thiuronium chloride was synthesized. It was shown that this polysiloxane, which is neutral in aqueous solution, imparted durable water resistance to fabrics with alkali treatment, heat treatment, or aging. The water resistance and durability is mainly due to formation of insoluble trifunctional methylpolysiloxane resin on the surface of the fabric.

### I. Introduction

Since Winton I. Patnode obtained the first patent [14] on the water repellency of organic silicon compounds in 1942, several hundred organic silicon water repellents have been reported in the literature and patents, and many commercial products have been put on the market. These commercial organic silicon water repellents are roughly classified as follows: (1) organochlorosilanes, (2) diorganopolysiloxanes, (3) methylhydrogenpolysiloxane, (4) organopolysiloxane resins, (5) sodium methylsiliconate.

Methylchlorosilanes—typical of the monomeric organic silicon water repellents, such as organochlorosilanes—give durable water repellency without heat treatment or curing [2, 5, 9, 15], but their application for organic fabrics is impracticable because of evolution of hydrogen chloride. At present their application is practically limited to inorganic materials such as glass and ceramics. Dimethylpolysiloxane, typical of linear diorganopolysiloxanes, also imparts durable water repellency, but it requires heat treatment over 200° C. [6, 12, 15]. Methylhydrogenpolysiloxane has been most widely used as a commercial silicone water repellent for organic fabrics because it imparts durable water repellency with heat treatment at about 150° C. [4, 7, 12]. Methylpolysiloxane resin, which is typical of trifunctional organopolysiloxane resins, has been generally used as an air-drying-type water repellent for organic fabrics, because it imparts good water repellency without heat treatment [3, 7]. But in general its water repellency is not durable to soap washing and/or dry cleaning [11]. Sodium methylsiliconate [7], the only water-soluble silicone water repellent, also cannot be applied to most organic fabrics, since its aqueous solution becomes strongly alkaline.

Recently, a water-soluble methylpolysiloxane containing thiuronium chloride and neutral in aqueous solution, was synthesized by the authors. It was found that this polysiloxane imparts durable water repellency to fabrics with alkaline treatment or aging and requires no heat treatment. These properties make this type of compound of definite interest. In this paper, the water repellency of polysiloxane, applied to silk and cotton, has been reported, although the results obtained are qualitative.

### II. Preparation and Properties of Methylpolysiloxane Containing Thiuronium Chloride

The preparation and properties of methylpolysiloxane containing thiuronium chloride, previously reported in detail by one of the authors [13], are de-

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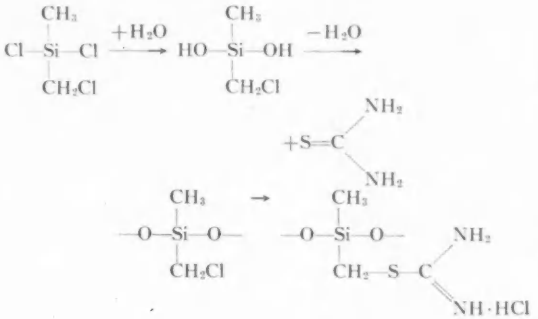
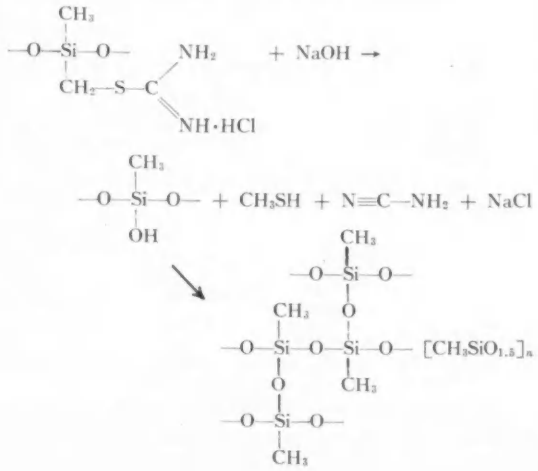
scribed below. The polysiloxane is quantitatively prepared by reaction of thiourea and chloromethylmethylpolysiloxane in alcohol medium, which is obtained by hydrolysis of chloromethylmethyldichlorosilane.



This thiuronium polysiloxane, a glassy solid, is soluble in water, and neutral in aqueous solution. It is stable to heating in both neutral and acid solutions. Upon adding alkali to the aqueous solution, however, a white amorphous precipitate is produced, with an evolution of methyl mercaptan. Probably the fission of silicon-carbon linkage is caused in the first place, followed by the usual fission of sulfur-carbon bond, and the immediate condensation of the newly formed silanol to give a new siloxane linkage. The composition of the precipitate is the same as that of the trifunctional methylpolysiloxane resin, $CH_3SiO_{1.5}$, obtained with hydrolysis and dehydration-condensation of methyltrichlorosilane, $CH_3SiCl_3$.



## III. Experimental

### 1. *Fabrics*

In this experiment a commercial silk fabric (Kanegabuchi Spinning Co., Ltd., "Fujiginu," No. 5000) and a cotton calico (Kanegabuchi Spinning Co., Ltd.) were used. The specimens were pretreated as follows: The silk fabric was thoroughly washed with a hot soap solution, then extracted with ether for 2 hr. (about 40 cycles) by using a Soxhlet extractor, and air-dried. After desizing, the cotton fabric also was extracted with ether by the same method as silk, and then air-dried.

### 2. *Compound Investigated*

Methylpolysiloxane containing thiuronium chloride was synthesized by the authors. The mean polymerization degree of the chloromethylmethylpolysiloxane used for the synthesis was 17, and the molecular weight was 1810.

### 3. *Dipping*

The pretreated specimens were immersed in an aqueous solution of thiuronium polysiloxane for 30 min. at room temperature, and air-dried with no squeezing. The bath ratio was about 20 to 1 in any case.

### 4. *Alkali Treatment*

Although the thiuronium polysiloxane is easily decomposed with alkali such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, or sodium bicarbonate, in this experiment ammonia, either in aqueous solution or as a vapor, was employed. The specimens treated with the polysiloxane were either immersed in an aqueous solution of ammonia, or exposed to vapor of ammonia in a desiccator. They were held at the upper part of the desiccator so as not to touch the 30% ammonia solution in the bottom.

### 5. *Curing Treatment*

For the curing of the treated specimens, a hot air-type oven was used. The conditions were as follows: time, 10 min., temperature, 50°, 100°, 150°, 200° (±2°) C; speed of hot air, about 2 meters/sec. After air-drying for a day at room temperature, the treated specimens were directly heat-treated under the above conditions.

*6. Aging*

In order to investigate whether or not water repellency is affected by aging, the following experiment was made. Applying no alkali, the specimens treated with polysiloxane, with or without heat, were left for some days at room temperature, and then the water repellency was measured.

*7. Measuring of Water Repellency*

In these tests the hydrostatic pressure method of the American Association of Textile Chemists and Colorists [1] was employed as a measure of the resistance of treated fabrics to the penetration of water, termed in this paper "water repellency."

*8. Durability to Solvent*

As a method of estimating the durability to solvent dry cleaning, the following experiment was made. After measuring the hydrostatic pressure, the treated specimens were extracted with ether in a Soxhlet extractor for 2 hr. (about 40 cycles), then air-dried, and again tested for hydrostatic pressure. The reason for using ether is that in general ether is a good solvent of difunctional linear diorganopolysiloxanes, such as dimethylpolysiloxane and methylhydrogenpolysiloxane, and perfectly trifunctional organopolysiloxane resins are insoluble in ether.

In some cases, the treated specimens were mechanically shaken in perchloroethylene or n-hexane for 1 hr. instead of ether extraction.

## IV. Results

*1. Ammonia Treatment*

The water resistance of silk treated with ammonia after immersing in 1% aqueous solution of the thiuronium polysiloxane is shown in Figure 1. First, immediately after the polysiloxane treatment, the specimens were immersed in 3% ammonia solution with stirring for 10 min., then given two 10-min. rinses in water, after which they were air-dried for a day and heat-treated. *A* indicates the hydrostatic pressure of the specimens treated as above mentioned. A slight water resistance was obtained with curing. Second, after the polysiloxane treatment and air-drying for a day, the specimens were immersed in 3% ammonia solution with stirring for 10 min., then air-dried for a day with no rinsing, and heat-treated (shown in *B*). It will be seen that even less water resistance was imparted by curing. Third, after the polysiloxane treatment and air-drying, the specimens were dipped for a moment in 1% ammonia solution, then air-dried for a day, and heat-treated (shown in *C*). In this case, water resistance strikingly increased with a rise in temperature of curing. Fourth, after the polysiloxane treatment and air-drying, the specimens were exposed to ammonia vapor for a day, then air-dried, and heat-treated (shown in *D*). It is evident that no heat treatment was required in order to impart excellent water resistance to the fabrics. The most effective procedure involves applying the polysiloxane and giving the treated fabric an alkaline exposure without removing the water-soluble polysiloxane.

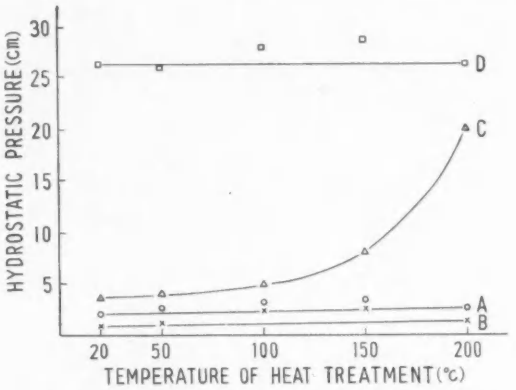



**Fig. 1.** Water resistance of silk treated with thiuronium polysiloxane.

The water resistance of cotton calico treated with ammonia after being immersed in 1% aqueous solution of thiuronium polysiloxane is shown in Figure 2.

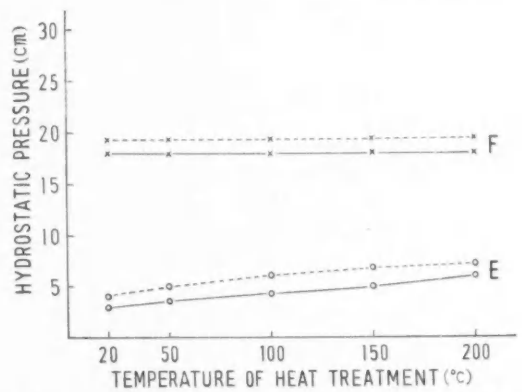



**Fig. 2.** Water resistance of cotton treated with thiuronium polysiloxane. Dotted lines = after ether extraction.

*E* illustrates the hydrostatic pressure of the specimens, immersed in 1% ammonia solution and then heat-treated. The water resistance imparted was similar to that shown in *A* and *B* in Figure 1. *F* indicates the hydrostatic pressure when ammonia is used in vapor form instead of in solution. In this case, excellent water resistance was obtained with no heat treatment; the fabric was durable to ether extraction for 2 hr.

The following additional durability tests were tried. Silk specimens were treated with 3% aqueous solution of thiuronium polysiloxane, then air-dried, and exposed to ammonia vapor, applying no heat treatment. Following this, the hydrostatic pressure of the specimens so treated was measured before and after perchloroethylene- or n-hexane shaking. The results of these tests show that excellent water resistance, durable to perchloroethylene- and n-hexane cleaning, is imparted to silk without heating (Table I).

**TABLE I. Hydrostatic Pressure Test of Silk Treated with 3% Aqueous Solution of Thiuronium Polysiloxane**

| | n-Hexane (cm.) | Perchloroethylene (cm.) |
|---|---|---|
| Before dry cleaning | 24.0 | 24.0 |
| After dry cleaning | 23.8 | 24.4 |

*2. No Alkali Treatment*

*G* and *H* in Figure 3 show the water resistances of silk treated with 3% polysiloxane solution and then heat-treated, omitting ammonia after-treatment. These results indicate that excellent water resistance, durable to ether extraction, can be obtained with curing only.

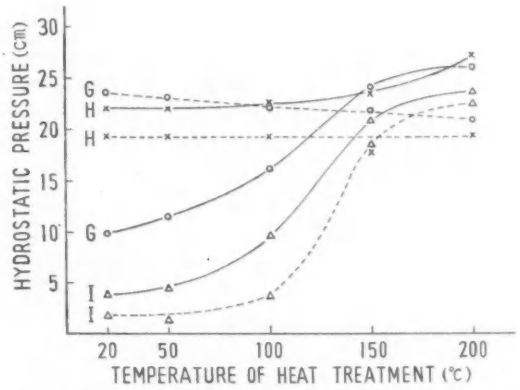



**Fig. 3.** Water resistance of silk treated with thiuronium polysiloxane and methylhydrogenpolysiloxane. Dotted lines = after ether extraction.

*3. Aging*

In Figure 3 the only difference in procedure between *G* and *H* is the period of time during which the specimens treated with the polysiloxane were left at room temperature prior to the hydrostatic pressure test after heat treatment. In the case of *G*, the treated specimens were left for 3 days, and *H*, 15 days. Comparing *G* and *H*, therefore, it will be seen that water resistance rises gradually when the specimens remain at room temperature for a long time after the polysiloxane treatment. This tendency is clear in the low-temperature curing region of 50° or 100° C.

For comparison, the water resistance of the same silk treated with 1% carbon tetrachloride solution of methylhydrogenpolysiloxane is also shown in Figure 3. *I* illustrates the hydrostatic pressure measured the day after the curing treatment. The water resistance of fabrics treated with methylhydrogenpolysiloxane is also affected by aging [12].

## V. Discussion

In general, water repellency is recognized as one of the unique properties peculiar to organic silicon compounds, but there have been few reports concerning the mechanism of their water repellency. Hunter [6], Warrick [16], and McGregor [8] have explained the mechanism of water repellency of dimethylpolysiloxane as follows. This compound has an external structure similar to paraffin hydrocarbon, formed by orientation of methyl groups attached to each silicon atom. From their investigation on water-repelling treatment of fabrics with methylchlorosilanes [9] and methylhydrogenpolysiloxane [10, 12], the authors have drawn the conclusion that the formation of cross-linking with an oxygen bridge, that is, a network structure, is one of the most important factors in the water resistance of the treated fabrics, so far as methylpolysiloxanes are concerned. Recently Fortess [4] and Kather [7] have presented a similar concept on the water repellency of methylhydrogenpolysiloxane. As already demonstrated, a trifunctional methylpolysiloxane resin may be obtained by alkali decomposition of a water-soluble methylpolysiloxane containing thiuronium chloride.

From this it would appear that it must be possible to impart water repellency by carrying out alkali decomposition of the polysiloxane on the surface of fabrics, even without heat treatment. This concept is supported by the results of this study in which excellent water resistance has been obtained on fabrics treated with thiuronium polysiloxane.

*1. Ammonia Treatment*

In the cases of *A*, *B*, and *E* (Figures 1 and 2), a very slight water resistance is obtained with heat treatment. This is caused by the release of methylsilanol, an intermediate of trifunctional methylpolysiloxane resin, formed by the decomposition of thiuronium polysiloxane from fabrics upon stirring in ammonia solution or rinsing with water. In the case of *C* from 100° C., the water resistance increases remarkably with rising temperature of heat treatment. This may be mainly due to acceleration of dehydration-condensation reaction with heating, that is, conversion of water-soluble methylsilanol to the trifunctional methylpolysiloxane water-repellent resin on the surface of fabric. In the cases of *D* and *F*, durable water resistance is imparted with no heat treatment. The reason probably is that the employing of ammonia vapor instead of aqueous solution not only prevents the removal of methylsilanol from fabric, but facilitates the dehydration-condensation reaction. The durability to ether extraction as shown in *F*, and to percholoethylene- or n-hexane shaking, as shown in Table I, appears to be based on the formation of insoluble trifunctional methylpolysiloxane resin around each fiber.

*2. No Ammonia Treatment*

In the cases of *G* and *H* in Figure 3, the formation of insoluble trifunctional methylpolysiloxane resin on the surface of fabric would be a main reason for the water resistance and the durability to solvent. The curing treatment is supposed to accelerate the formation of trifunctional resin. In view of the stability of a neutral aqueous solution of the thiuronium polysiloxane to heating, however, the exact mechanism of these phenomena is open to discussion.

## VI. Summary

A water-soluble methylpolysiloxane, containing thiuronium chloride, was shown to impart durable water resistance to fabrics with either alkaline treatment, heat curing, or aging. The water resistance and durability is mainly due to the formation of insoluble trifunctional methylpolysiloxane resin on the surface of fabrics.

## Acknowledgment

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# Determination of the Degree of Crystallite Orientation in Cotton Fibers by Means of the Recording X-Ray Diffraction Spectrometer

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**Abstract**

An improved technique is described for the quantitative determination of the degree of crystallite orientation of cellulose in cotton and related cellulosic fibers, using the X-ray diffraction spectrometer with potentiometer recording and a rotating specimen mount.

The method is based on the angular dispersion of the 002 diffraction arc of cellulose but employs the somewhat more conveniently determined angle at half-maximum intensity instead of the photographically determined "40% angle," used by Berkley.

It is shown that the angle of half-maximum intensity (50% angle by analogy) is less than Berkley's "40% angle" by a constant value of 3.3°.

The effects upon the precision of the results of sample preparation and instrumental variations are described. Under the conditions proposed, the precision of the half-maximum angle is about 0.65°. This compares with a precision of about 1.0° for results obtained by photographic recording and photometering of the X-ray patterns [2].

Using the improved X-ray spectrometer technique described, the dark room required for photographic determination of orientation, with its rigid processing control, can be dispensed with, and a determination can be made in about one-fourth of the time.

## Introduction

In an earlier paper, Segal, Creely, and Conrad [10] have shown that a recording Geiger counter X-ray spectrometer may be used in the quantitative determination of the degree of orientation of cellulosic and other textile fibers. They stated that with this instrument a considerable saving of time can be realized by replacing the conventional photographic plate with a Geiger counter, and thereby eliminating the need for a darkroom and its equipment. They described a rotating specimen holder for use in making X-ray tracings and showed tracings which give essentially the same information as that usually obtained by photographing the X-ray diffraction patterns and photometering the patterns.

Irvin and Breazeale [6] built a rotating sample holder similar to that described by Segal, Creely, and Conrad [10] and used it on a high-angle recording spectrometer to measure the degree of crystallite orientation in rayon tire cords.

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As has been shown by Meyer and Mark [9], the most intense interferences from native cellulose are from the 002 planes; these planes are orientated parallel to the long axis of the crystallite. Each of these planes, which is at an angle $\theta$ to the X-ray beam and fulfills the conditions of the Bragg equation, $n\lambda = 2d \sin \theta$, diffracts X rays to give the 002 diffraction arc at right angles to the long axis of the crystallite. A photographic recording of the diffraction arc represents, therefore, a summation of the individual diffractions from the 002 planes of all the diffracting crystallites, and a comparison of the intensity distribution around the arc thus gives a measure of the orientation of the crystallites.

An empirical X-ray method for quantitative comparison of crystallite orientation in cellulose fibers was first developed by Sisson and Clark [13]. They obtained X-ray fiber patterns of combed fiber bundles on flat photographic plates and, using a microdensitometer, derived intensity distribution curves from the fiber patterns by measuring the optical density around the 002 diffraction arc. A relative value was thus obtained for the number of crystallites at various

angles to the fiber axis. An extensive study was made by Sisson [11, 12] of the crystallite orientation in cellulosic fibers and membranes, and of the relationship between this parameter and tensile strength.

The advantages and limitations of the X-ray method as a means of estimating the strength of raw cottons were reported by Conrad and Berkley [4]; and this method after some further refinements and standardization was later used by cotton breeders and fiber technologists [2] of the U.S. government in its cotton variety reports. The laborious measurement of the degree of blackening in the photographic plate was improved somewhat with the development of a special microphotometer by Berkley and Woodyard [1]. This did much toward establishing the X-ray method as a standard method for fiber evaluation. Later work by Tsien [15] verified the selection of the 002 plane as that most practicable for the purpose, although theoretically not entirely appropriate.

Meredith [8] further improved this technique by using a calibration strip on each film. This allowed direct conversion of the microphotometer readings into the corresponding X-ray intensities. It was claimed that this eliminated variations in film opacity as well as instrumental effects.

The direction measurement of X-ray intensities by means of the Geiger counter technique, as compared with photographic recording, was found by Buhler [3] to result generally in a saving of time, in greater simplicity of operation, greater sensitivity, and improved accuracy of results. The X-ray spectrometer, used with specially developed specimen mounts, has been applied to the determination of preferred orientations in materials by a number of workers, among them, Decker, Asp, and Harker [5]; and Jetter and Borie, Jr. [7].

The present paper more fully describes the instruments and technique first outlined by Segal, Creely, and Conrad [10] for measurement of crystallite orientation in cotton fibers. Its purpose is to explore the effects of sample preparation and instrumental variations upon the precision of the results and to compare the spectrometer results with those obtained photographically.

## Experimental Procedure

The principle of the method is based upon the assumption, previously outlined by Sisson and Clark [13] and applied to the photographic method, that the distribution of diffraction intensity around the 002 arc is perpendicular and proportional to the distribution of the long crystallite axes along the specimen (fiber bundle) irradiated by the primary X-ray beam. In the method to be described, the photographic film is replaced by a Geiger counter. The impulses from the latter are fed into a recording potentiometer; the amplitude of the curve thus traced is proportional to the intensity of diffracted radiation received by the Geiger counter. Rotation of the fiber bundle in a plane at right angles to the X-ray beam causes the diffraction arcs of the 002 plane to rotate before the window of the Geiger counter. Rotation is accomplished by means of the rotating specimen mount previously described by Segal, Creely, and Conrad [10].

During the period of time that these data were being collected, the instrument was modified in connection with other work by placing Soller slits [14] before the X-ray port and before the Geiger tube. Thus, part of the data used in the present report were obtained using Soller slits, and part, without. Although the use of Soller slits was found to increase the degree of resolution and to reduce background scatter, their use did not appreciably alter the half-maximum angle (defined later) obtained with the regular slits. In the absence of Soller slits, a slit system of $0.8 \times 1.8$ mm. was placed at the X-ray port and an opening $1.0 \times 3.0$ mm. was used in front of the Geiger tube. When the Soller slits were used, the incident beam was limited by a slit $1.2 \times 12$ mm. The beam to the Geiger tube was defined by two slits which were separated from each other by about 50 mm.; the most distant slit from the tube was $0.7 \times 12$ mm., the nearest $0.4 \times 12$ mm. The incident beam was also limited by the circular opening, 6 mm. in diameter, in the rotating specimen mount through which it passed. A nickel foil was used before the Geiger tube to absorb most of the K-beta radiation.

Except for the results comparing the Geiger counter and photographic methods (Table V), and those shown in Figure 3, the data reported were all obtained from the same sample of Stoneville 2B cotton.

### *Sample Preparation*

A representative subsample was obtained by taking small pinches of fiber at random from the large sample. This subsample was drawn between the fingers

into a hand sliver. It was then combed into a flat bundle of parallel fibers by combing each end from the middle outward, giving each side 15 strokes on a coarse comb. Each end was then combed 20 strokes on a fine comb. The bundle size was adjusted so that its weight was 0.030 ± 0.001 g./in.

The fiber bundle was next placed upon the combs of the rotating specimen mount previously referred to [10] with the two combs in close contact. The combs were then moved apart to a distance of $\frac{3}{8}$ in., thus producing a flat parallel bundle, and the upper jaws of the clamp were fastened down upon the fibers, thus holding them securely in the comb. The springs for applying a uniform predetermined tension upon the fiber bundle were then set in place between the combs. Finally, the bundle was accurately aligned so that its center would coincide with the center of the X-ray beam.

*Recording the Diffraction*

The $2\theta$ angle at which the 002 plane diffracts was first accurately located by making a radial scan with the fiber bundle held vertically. Figure 1 shows a typical tracing obtained in this manner. The goniometer position which gave maximum intensity was noted and the Geiger counter set at this position. The radiation diffracted along the 002 arc was thus intercepted by the Geiger counter and its intensity recorded upon the potentiometer chart, giving the azimuthal scan. A synchronous electric motor with an output shaft speed of 1/15 r.p.m. was so geared to the rotating bundle holder that the bundle made one complete revolution every 30 min. With the goniometer set at the proper angle and the X-ray beam turned on, the specimen holder and the recorder were started simultaneously. With the recorder set to move at a chart speed of $\frac{1}{2}$ in./min., the bundle, making one complete revolution in 30 min., produced two peaks and two valleys upon a 15-in. length of chart.

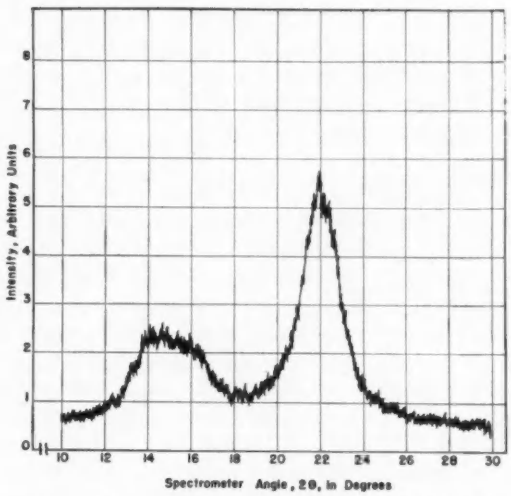


**Fig. 1.** Radial scan of cotton fiber bundle with fibers in vertical position.

*Measurement of Half-Maximum Angle*

Evaluation of the tracing obtained upon the chart was done in a manner somewhat similar to that described by Berkley [1, 2] for the microphotometer tracing in the photographic method, except that the half-maximum angle (angle subtending point of 50% of maximum intensity) was generally used instead of the "40% angle" (angle for 40% of maximum intensity).[2] The angle between the position of maximum intensity of the 002 arc and that of one-half maximum intensity is taken as a relative measure of the degree of orientation. The method of measurement on an azimuthal tracing is illustrated in Figure 2, where the peak was obtained by rotation of the fiber bundle through 180°. One line is drawn tangent to the valleys of the curve (0° and 180°), and a second line is drawn through the mean maximum point of the peak ($B$), parallel to the lower line. The line $BE$ is dropped from $B$ perpendicular to the lower line, and for the half-maximum angle, the line $CD$ is drawn at half the height of $BE$ ($EO = \frac{1}{2}\ BE$) parallel to the upper and lower lines. The average angular distance from $BE$ to the points $C$ and $D$ on the legs of the curve is the half-maximum or 50% angle of orientation. The 40% angle is obtained by placing the line $CD$ at 0.4 of the height of $BE$ ($EO$ now becomes 0.4 $BE$) and measuring the angular distance as above.

Tracings of two samples of cotton showing wide extremes in relative degree of orientation are recorded with maximums superimposed in Figure 3. The lines $C$-$D$ and $C'$-$D'$, connecting the points of half-maximum intensity on each side of the peak, represent in the two samples angles of crystallite orientation of 27.6° and 42.6°, respectively.

With the spectrometer, measurements of two half-

[2] The half-maximum angle was chosen instead of the 40% maximum angle in view of its wide acceptance and use by physicists for line width measurements in X-ray and other work.

maximum angles may be obtained from a single bundle within a period of 1 hr.; this includes time for preparing the bundle, recording the diffraction, and measuring the chart. For the photographic method, approximately 7 hr. are required for bundle preparation, exposure, development, microphotometering, and measuring the 40% angle. With two bundle holders and proper programming of operations, one operator using the spectrometer could complete about four samples of two bundles each per day.

*Comparison of Results with Photographic Measurements*

Photographic measurements of the X-ray angles of various cottons were made by the staff of the Field Crops Research Branch (formerly the Division of Cotton and other Fiber Crops and Diseases, Bureau of Plant Industry, Soils and Agricultural Engineering), using the standard photographic technique [2]. The identical fiber bundles used by these workers were not available for the present spectrometer study, but the same lots of cotton from which these bundles were drawn were still available for further sample preparation. Not having the same fiber bundles for examination was not considered to be serious, since

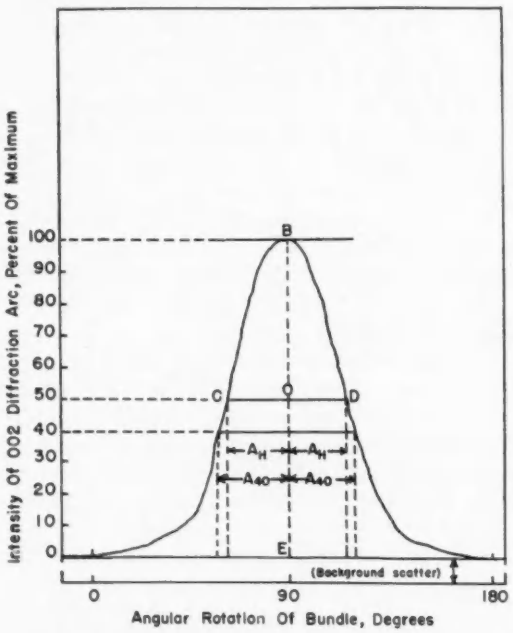


**Fig. 2.** Measurement of half-maximum angle.

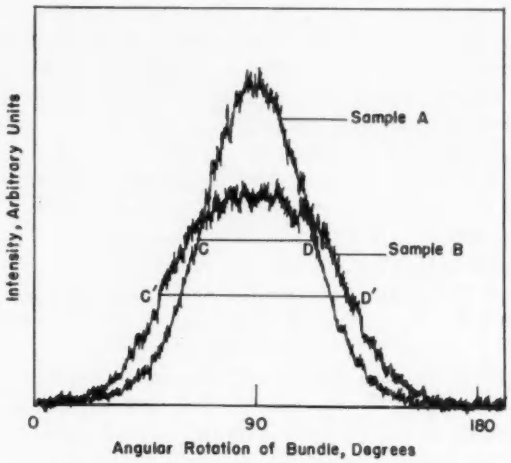


**Fig. 3.** Azimuthal X-ray tracings of the 002 arcs of cotton samples with relatively high ($A$) and low ($B$) degree of crystallite orientation.

in the photographic technique itself a standard error of $\pm 1.0°$ in the data was recognized as conservative by Berkley and co-workers [2]. This was based on approximately 2000 observations made by different operators and using a wide range of photographic intensities. The 40% angle was computed on the spectrometer tracings of these samples in addition to the half-maximum angle to permit comparison with the 40% angle of the samples obtained by the photographic method.

## Results and Discussion

The precision of the results obtainable is limited by two general factors: instrumental and bundle preparation. The influence of each of these factors on the results is discussed below.

*Reproducibility of Recordings*

The data given in Table I were obtained from three fiber bundles from the same gross sample. The bundles were allowed to rotate through four revolutions so that eight peaks were recorded for each bundle. The data were subjected to an analysis of variance with results as shown in the lower part of the table. It is observed that significant variations are associated with bundle preparation and peak measurements. No significant variations were associated with successive revolutions. Bundle variance doubtless comes partly from lack of randomness in fibers and partly from nonuniform preparation.

**TABLE I. Reproducibility of Measurements**

| Bundle number | Revolution number | Half-maximum angle in degrees | | |
|---|---|---|---|---|
| | | Peak A | Peak B | Mean |
| I | 1 | 25.3 | 24.6 | |
| | 2 | 26.0 | 25.2 | |
| | 3 | 26.0 | 25.9 | |
| | 4 | 25.7 | 25.8 | 25.6 |
| II | 1 | 26.0 | 25.4 | |
| | 2 | 26.0 | 25.4 | |
| | 3 | 25.7 | 25.4 | |
| | 4 | 25.4 | 25.2 | 25.6 |
| III | 1 | 24.6 | 25.9 | |
| | 2 | 24.6 | 24.6 | |
| | 3 | 24.7 | 25.4 | |
| | 4 | 25.5 | 25.1 | 25.0 |
| Grand mean | | | | 25.4 |

**Analysis of Variance**

| Source | Sum of squares | Degrees of freedom | Mean square |
|---|---|---|---|
| Bundles | 1.77 | 2 | 0.885* |
| Revolutions | 1.81 | 9 | 0.201 |
| Peaks | 1.20 | 3 | 0.400† |
| Residual | .87 | 9 | 0.097 |
| Total | 5.65 | 23 | 0.246 |

* Significant at 1% level.
† Significant at 5% level.

Peak variation comes most likely from nonuniform bundles and lack of exact centering.

*Effect of Beam Size*

The effect of minimum and maximum (0.8 × 1.8 to 1.5 × 3.8 mm.) beam size at the X-ray port was determined on three bundles. The slit size before the Geiger counter was 1 × 3 mm. The results are presented in Table II, where each average represents four observations. Considering the mean values of the half-maximum angles of the samples, it is apparent that the magnitude of any difference in values due to use of different slit sizes is small and approximates the difference associated with bundle preparation. One bundle was examined with Soller slits in place and the results are included for comparison. Further comparison may be made by referring to the results in Table III.

*Variations Due to Normal Bundle Preparation*

To obtain a better idea of the principal sources and magnitudes of errors, the average half-maximum angles were determined for ten bundles prepared in the normal manner (see above). Soller slits were used. The half-maximum angles were recorded for each bundle over two revolutions of two peaks each. The results, together with an analysis of variance, are presented in Table III.

**TABLE II. Effect of Slit Size at X-Ray Port on Mean Half-Maximum Angle**

| Bundle No. | Slit size | | | |
|---|---|---|---|---|
| | 0.8×1.8 mm. | | 1.5×3.8 mm. | |
| | Degrees* | Standard deviation | Degrees* | Standard deviation |
| 1 | 25.3 | 0.6 | 25.2 | 0.5 |
| 2 | 24.2 | 0.3 | 25.1 | 0.8 |
| 3 | 24.1 | 0.6 | 24.1 | 0.8 |
| | Soller slits 1.2×12 mm. | | | |
| 4 | Mean | | 25.6° | |
| | Standard deviation | | 0.3 | |

* Each mean based on four peaks.

**TABLE III. Influence of Normal Sampling and Bundle Preparation on Mean Half-Maximum Angle**

| Bundle No. | First revolution | | Second revolution | | Mean angle deg. |
|---|---|---|---|---|---|
| | Peak A deg. | Peak B deg. | Peak A deg. | Peak B deg. | |
| 1 | 24.1 | 24.4 | 24.5 | 24.8 | 24.5 |
| 2 | 24.2 | 25.2 | 24.7 | 25.1 | 24.8 |
| 3 | 25.0 | 25.7 | 25.6 | 25.3 | 25.4 |
| 4 | 25.2 | 26.0 | 24.6 | 25.8 | 25.4 |
| 5 | 25.0 | 24.6 | 25.1 | 25.4 | 25.0 |
| 6 | 25.9 | 25.7 | 26.4 | 25.9 | 26.0 |
| 7 | 25.0 | 25.0 | 25.2 | 25.0 | 25.1 |
| 8 | 24.0 | 24.5 | 24.7 | 24.6 | 24.5 |
| 9 | 25.2 | 24.2 | 25.2 | 25.0 | 24.9 |
| 10 | 25.2 | 24.2 | 25.1 | 25.6 | 25.0 |
| Grand mean | | | | | 25.1 |

**Analysis of Variance**

| Source | Sum of squares | Degrees of freedom | Mean square |
|---|---|---|---|
| Bundles | 7.63 | 9 | 0.85* |
| Revolutions | 1.45 | 10 | 0.15 |
| Peaks | 2.21 | 10 | 0.22 |
| Residual | 1.35 | 10 | 0.14 |
| Total | 12.64 | 39 | 0.32 |

* Significant at 1% level.

From Table III it can be seen that bundle preparation and selection is the principal and only significant source of definable error. Successive revolutions, i.e., more than 360°, are obviously unnecessary. Peak variation is again the second highest source of error, although in this experiment the effects were not statistically significant. Perhaps the bundle density was more uniform and the centering more adequate.

Under the assumption that a standardized technique will include two peaks (one revolution) from each of two bundles per sample, a summated standard error of 0.65°/sample can be computed. This is confirmed almost exactly by similar computations, based on the data of Table V, as well as on other data not included in the present study. The technique, including bundle preparation, centering, and recording, requires about 2 hr./sample or about one-third that required by the photographic method.

*Effect of Tension on Fibers*

Although no provision was made for variation of tension in the rotating specimen mount, it has been possible to study the effect of tension indirectly by varying the size of the bundles, thereby redistributing the stress per fiber. The springs used apply about 1800 g. total tension between the jaws. In Table IV is shown the effect upon half-maximum angle of variation of bundle weight at this constant tension. The different bundles were prepared from the same sample. The data confirm the fact observed earlier [2], that the X-ray angle is affected by the amount of tension applied to the fiber. However, since bundle weight normally does not vary by more than ± 0.001 g., the magnitude of the effect is so small as to be of little influence upon the value obtained for the half-maximum angle.

**TABLE IV. Effect of Mean Tension per Fiber upon Half-Maximum Angle**

| Weight of bundle, g. | Estimated tension per fiber, g. | Mean half-maximum angle* | |
|---|---|---|---|
| | | Degrees | Standard deviation |
| 0.010 | 0.75 | 21.9 | 0.4 |
| 0.014 | 0.53 | 22.5 | 0.7 |
| 0.016 | 0.47 | 24.3 | 0.5 |
| 0.025 | 0.30 | 25.6 | 0.5 |
| 0.029 | 0.26 | 25.6 | 0.6 |
| 0.034 | 0.22 | 26.1 | 0.2 |
| 0.043 | 0.17 | 26.1 | 0.3 |

* Each mean based on 4 peaks.

The tension for the Stoneville 2B cotton has been calculated as 0.250 g./fiber for the size of bundle normally used, i.e., 0.030 g./in. of length, and with 1800 g. of tension on the bundle. This tension is approximately 5% of the average breaking load of the fibers.

*Comparison with Results Obtained Photographically*

The 40% angles of the spectrometer tracings were determined for 11 commercial varieties. They are compared in Table V with the 40% angles obtained in the usual manner by the photographic method and also to the half-maximum angles. The photographic measurements for the samples of Stoneville 5, Missdel 4, and Qualla, listed in Table V, were taken from a report of a variety study [16]. The other photographic values listed for comparison in Table V were supplied by other workers, for whom spectrometer measurements were made. The varieties of Controls A and B are not known. However, they are described as such since they are the control samples for the Defoliated A and B samples reported on. The means of angles by the two methods for the 11 samples differ by less than 0.1° and hence are considered for all practical purposes to be equal. The correlation coefficient was 0.978; and the regression equation

$$A_P = 1.63 \pm 0.954\ A_G$$

where $A$ is the X-ray angle and the subscripts $P$ and $G$ refer to photographic and Geiger counter methods of recording, respectively. Based on the above equation, the X-ray spectrometer method would give

**TABLE V. Comparison of Photographic and Geiger Counter Data**

| Sample | 40% Angle | | Half-maximum angle Geiger counter,* deg. |
|---|---|---|---|
| | Photographic, deg. | Geiger counter,* deg. | |
| Stoneville 5 | 28 | 27.6 | 24.0 |
| Defoliated A | 31.2 | 30.8 | 27.5 |
| Control B | 32.7 | 31.3 | 28.3 |
| Control A | 30.8 | 31.5 | 27.6 |
| Rowden 41 B | 32.6 | 31.8 | 28.2 |
| Defoliated B | 33.2 | 32.5 | 29.1 |
| Seaberry Sea Island | 32.2 | 32.6 | 29.3 |
| Tanguis | 33.0 | 34.6 | 31.5 |
| Mesa Acala | 34.6 | 35.1 | 32.1 |
| Missdel 4 | 41 | 40.0 | 36.6 |
| Qualla | 42 | 42.6 | 38.9 |
| Mean of techniques | 33.8 | 33.7 | 30.3 |

* Each mean based on four observations.

values 0.7° greater than the photographic method at X-ray angles of 20° and 0.2° less at 40°. In view of the small errors associated with both methods these differences are again not considered significant. These conclusions are in agreement with those of Irvin and Breazeale [6] regarding the equivalence of results obtained by the two techniques.

*Relation of Half-Maximum to 40% Angle*

In order that the half-maximum angle of the X-ray spectrometer may be most serviceable, its relation to the 40% angle must be established. Since in the preceding section the 40% angles, determined with the X-ray spectrometer, were shown to be essentially equivalent to those obtained by microphotometering the photographic X-ray patterns, it was considered to be adequate merely to establish the relationship between the angles determined with the aid of the spectrometer at the 40% and half-maximum positions. The half-maximum angles are also presented in Table V. The regression equation was found to be

$$A_H = 0.997\ A_{40} - 3.3$$

where $A$ refers to the X-ray angle and the subscripts, $H$ and 40, refer to the angle of half-maximum and 40% maximum intensity, respectively, of the 002 diffraction arc. The standard error of estimate was found to be 0.3°. From the above equation it is evident that the half-maximum angle differs from the 40% angle by a constant value of 3.3°. This makes the conversion from half-maximum to 40% angles and the reverse exceedingly simple, by merely subtracting or adding the constant value to the angle determined at the other position.

## Conclusions

Measurements of the degree of crystallite orientation in cotton fiber bundles may be obtained, using the X-ray diffraction spectrometer with potentiometer recording and a rotating specimen mount.

Evaluation of the influence of instrumental and bundle preparation factors upon the results has shown that under favorable conditions a precision of about 0.65° (about 2%) can be achieved by the procedure recommended.

The effect of dimensions of slit at the X-ray port was found to be noncritical.

The half-maximum angle was influenced appreciably by varying the tension applied to the bundle in conformity with previous findings.

The results of Geiger counter and photographic techniques applied to a series of eleven cottons show that the X-ray angles at 40% of maximum intensity of the 002 arcs are essentially equivalent.

The half-maximum angles are smaller than those measured at 40% by a constant factor of 3.3°.

The half-maximum angles, representing degree of crystallite orientation in cotton and similar cellulosic fibers, can be measured with the recording X-ray spectrometer in about one-third of the time required for conventional photographic techniques and without the need for a dark room, with its requirements of rigid standardization, subsequent microphotometering of the film, and many of the uncertainties associated with photographic recording.

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# The Effect of Nuclear Radiation on Fibrous Materials

## Part I: Dacron Polyester Fiber[1]

**Otto Teszler and Henry A. Rutherford**

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**Abstract**

Dacron polyester filaments of different draw ratios were prepared and were exposed to high-energy radiation from two sources. Exposure both in a reactor and to a Cobalt-60 source resulted in an increase in the moduli of elasticity of the filaments. This indicated that cross-linking reactions took place and predominated over chain scission, particularly during the early stages of irradiation. Draw ratio, i.e., the degree of orientation of the filament, had an influence on the behavior. The materials of lower draw ratio tended to show more cross-linking than those of high draw ratio, the optimum being between 2.5:1 and 3.0:1. The degree of cross-linking in Dacron under the conditions of these experiments was, however, of a low order of magnitude. The solubility of the filaments was decreased only slightly, and the melting point remained unchanged. The degree of crystallinity of the filament did not influence the behavior of the filaments.

Although the work has not yet been extended to many other polymers, it is believed that materials which show a marked tendency to cross-link during exposure to high-energy radiation would show an effect similar to Dacron. For example, polyethylenes of different degrees of orientation or of different pretreatments might well behave quite differently with respect to changes in properties brought about by a given level of radiation. This has been partially substantiated by some preliminary results obtained with polyethylenes of unknown history, but at the same time known to be different in character prior to irradiation.

### I. Introduction

During the past several years, considerable interest has developed in the effects of high-energy radiation on polymers, particularly after it was learned that polyethylene could be made more resistant to heat by irradiation. It has been reported by others [1, 2, 6 through 10, 12], and substantiated by investigations carried out in this laboratory for the past two years, that the general effects of radiation on polymers are at least twofold: polymers may be improved with respect to certain properties through the medium of cross-linking or they may be degraded because of scission of their long-chain molecules. Thus, in one case, the effect is to increase the average molecular weight while in the other it is to decrease the molecular weight. Moreover, the properties of the irradiated materials indicate that both types of changes occur simultaneously but that in some polymers, at given levels of radiation, cross-linking reactions predominate, while in others degradation reactions are more in evidence.

In an effort to establish the nature of the behavior of polymers, Bopp and Sisman have irradiated a wide variety of plastics and elastomers in film form and have presented a rather complete report of their stability [1 through 5]. With some reservations as to the exact order, they ranked the polymer stability toward radiation according to chemical structure. It was clearly demonstrated that hydrocarbon long-chain polymers as such, or bearing no side-chains other than phenyl groups, were predominantly cross-linked. Thus, materials such as polystyrene and polyethylene showed the greatest stability toward radiation and the changes in physical properties suggested cross-linking. Cellulose, of special interest in the field of textiles, and materials containing fluorine or chlorine showed little resistance to chain cleavage and were near the bottom of the list with respect

[1] A product of E. I. duPont de Nemours & Co., Inc.

to radiation stability. Polyesters and polyamides showed intermediate orders of stability. It was recognized that there was some uncertainty as to the relative orders of stability of materials close together in the list as published by Bopp and Sisman, but it was implied that chemical structure was the deciding factor in behavior toward radiation. These investigators determined the effects of radiation on such properties as tensile, shear, and impact strengths; ultimate elongation; elastic modulus; hardness; specific gravity; and water absorption.

In a recent paper, Gilfillan and Linden [11] showed that cotton and viscose were less stable to neutron and gamma radiation than either nylon or Orlon.[2] These investigators used tenacity as the criterion for stability, and found no evidence of cross-linking in any of the materials.

During the course of some preliminary experiments in this laboratory relative to the effect of nuclear radiation on fibers, it was found that chemical structure was not the only factor that influenced stability. The present paper, which is the first in a series to appear from this laboratory, demonstrates that orientation also influences the behavior of fiber toward radiation. The work reported here deals with Dacron polyester fiber and in a future paper, it will be indicated that a polyamide responds in essentially the same manner, namely, that at lower levels of exposure, cross-linking tends to predominate to a greater extent in the unoriented materials.

## II. Materials and Methods

### *1. Identification and Handling of Samples*

The fibers used in this work were specially prepared by the Dacron Research Laboratory of E. I. du Pont de Nemours & Co., Inc. From the same polymer batch, fibers of different draw ratios were made in both dull and bright varieties. Two samples having a draw ratio of 3.5:1 were prepared, one being made under conditions known to give a crystalline-oriented polymer, while the other was drawn to give an amorphous-oriented polymer. The identification of the samples discussed in this paper is shown in the next column.

The continuous filaments were wound from cones in small skeins on a specially constructed skein winder. These skeins were folded several times and wrapped in thin, pure aluminum foil for exposure.

[2] Du Pont acrylic fiber.

| Sample No. | Luster | Draw Ratio |
|---|---|---|
| 1 | Bright | Undrawn |
| 2 | Bright | 2.5 |
| 3 | Bright | 3.0 |
| 4 | Bright | 3.5 |
| 5 | Bright | 3.5 (amorphous) |

Extreme care was taken to exclude all dirt, dust, and other impurities when the fibers were handled.

All samples were exposed to two sources of radiation at the Brookhaven National Laboratory. For neutron bombardment, a water-cooled exposure port (facility W-52) in the reactor was used. In this port the maximum prevailing temperature was approximately 40° C., and the flux consisted mostly of thermal neutrons. Samples were exposed for 1, 10, 100, and 1000 min. to obtain exposure levels of $10^{14}$, $10^{15}$, $10^{16}$, and $10^{17}$ n.v.t., respectively. The gamma irradiation was carried out using a Cobalt-60 source (facility 21-N). The samples were irradiated for 6 hr.-33 min., and 13 hr.-6 min. to obtain exposure levels of $5 \times 10^6$ and $1 \times 10^7$ roentgens, respectively.

The irradiated samples were received in vacuum-sealed containers. Prior to opening these containers, the activity at the surface was measured, and in some cases it was necessary to allow the samples to decay in radioactivity prior to testing. Techniques consistent with those required for handling radioactive materials were used throughout the work.

### *2. Melting Point*

The Fisher-Johns apparatus was used for determining the melting points of the various fiber samples. This equipment consists of a single aluminum casting containing an electrically-heated stage with controllable heat input. A depression in the casting permits the stable positioning of a small beaker or other receptacle. A small quantity of finely cut sample was placed between two clean microcover glasses (No. 2, 18 mm.), and these were pressed gently but firmly together and then placed in the circular depression on the stage. To maintain a constant pressure, a heavy washer-type weight was placed on the top of the cover glass. The instrument was turned on and the first run permitted to heat up rapidly to obtain an indication of melting point. Thereafter, the melting point was approached rapidly within 15°, then the Powerstat was turned down to permit a slow approach to the melting point. The samples were under constant observation, and all changes in physical appearance were noted.

*3. Solubility*

Solubilities of the filaments were determined in m-cresol. When the fibers were soluble at room temperature, the concentration of the solvent was decreased by the addition of a nonsolvent for Dacron and the solution then heated, if necessary, to solubilize the filament. The temperature at which the material dissolved was noted. In this way, small differences in solubility could be determined.

*4. Breaking Strength–Elongation*

The Instron Tester was used for the strength–elongation determinations, single filaments being used in each case. Statistical determinations were also made to obtain the number of tests required for each sample to give a reliable average. The modulus of elasticity was calculated from strength–elongation data at the yield point.

## III. Results and Discussion

Prior to the undertaking of the specific program that is described in this paper, over a year of preliminary work was conducted in order to establish the levels and conditions of exposure required to produce significant changes in the properties of the various fibrous materials. The preliminary work was done both at the Raleigh Research Reactor and at the Brookhaven National Laboratories. The results of this phase of the work, which are described briefly below, were used as a basis for the experiments described here and in the papers that are forthcoming from this laboratory.

First, the preliminary work showed that in order to avoid extensive radiation damage in the materials and to increase the possibilities of beneficial radiation effects, such as cross-linking, the fibers should be subjected to a flux of thermal neutrons rather than fast neutrons. Very short periods of exposure in a port where the ratio of fast to slow neutrons was high resulted in very high degrees of degradation. Because there is every reason to believe that the effect of thermal neutrons is essentially that of gamma rays,[3] it was decided to make a comparison of the effects of radiation containing both thermal neutrons and gamma rays (hereafter called neutron radiation) with the effects of gamma alone from a Cobalt-60 source. A second conclusion reached in the first phase of the work was that in the case of neutron radiation, the maximum desirable level of exposure was $10^{17}$ n.v.t. (the total neutron flux defined as the flux at the point of exposure in neutrons/sq. cm./sec. multiplied by the time of exposure in seconds). Thus, the present work was restricted to exposure at this level and below, namely, $10^{14}$, $10,^{15}$ and $10^{16}$ n.v.t. It was indicated in the present work that experimentation with intermediate as well as lower levels of exposure is in order. A third conclusion from the preliminary work was that excessive temperatures should be avoided in order to minimize the effects of temperature alone in the presence of radiation. Thus, a water-cooled exposure port for neutron radiation, where the average prevailing temperature was 35° to 40° C., was used.

Of primary interest in the present work was the question of whether or not cross-linking effects could be obtained by radiation of certain polymers and whether or not, as also indicated from preliminary work, the behavior might be influenced by the molecular orientation of the polymer. One means of evaluating cross-linking in fibers is by a study of the stress-strain characteristics. Bopp and Sisman [1 through 5], as well as Charlesby, have shown that the modulus of elasticity of polyethylene is increased by irradiation. The latter author demonstrated that as the radiation dose increased, the extent of cross-linking increased, and that there was a remarkable rise in Young's modulus with each increasing dose of radiation. Thus, when the slope of the curve obtained by plotting the moduli of elasticity as the ordinate against levels of radiation as the abscissa is positive, it is assumed that cross-linking has occurred. This is obviously a result of a stiffening of the polymer brought about by the bonding of adjacent molecules together by cross-linking. Moreover, it is assumed that when the slope of such a curve is negative, degradation of the long-chain polymer is the predominating effect, even though some cross-linking may be taking place. The application of this criterion for cross-linking or degradation was used in the present work. The changes in modulus at various levels of neutron and gamma irradiation, respectively, are shown in Figures 1 and 2. A logarithmic plot was used in Figure 1 and a semi-logarithmic plot in Figure 2.

[3] Slow or thermal neutrons are those with energies of about 0.025 electron volt and are captured by hydrogen atoms. The capture is immediately followed by the emission of a two-million electron-volt gamma ray, which, because of its high energy, can cause atomic disturbances and subsequent changes in the characteristics of the materials being exposed.

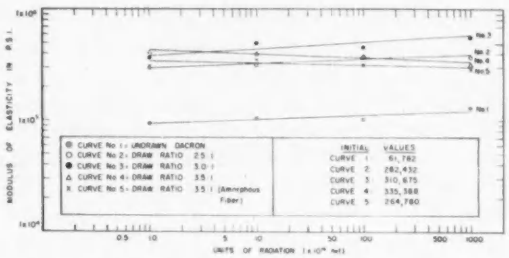
MODULUS OF ELASTICITY IN P.S.I.
UNITS OF RADIATION (x10^14 n.v.t.)
CURVE No. 1 = UNDRAWN DACRON
CURVE No. 2 = DRAW RATIO 2.5:1
CURVE No. 3 = DRAW RATIO 3.0:1
CURVE No. 4 = DRAW RATIO 3.5:1
CURVE No. 5 = DRAW RATIO 3.5:1 (Amorphous Fiber)
INITIAL VALUES
CURVE 1 61,782
CURVE 2 282,432
CURVE 3 310,675
CURVE 4 335,388
CURVE 5 264,780

**Fig. 1.** Effect of nuclear radiation on the modulus of elasticity of bright Dacron.

It may be noted first that at the lowest levels of exposure to neutrons ($10^{14}$ n.v.t.), and to gamma rays alone ($5 \times 10^6$ R), the moduli of elasticity of all the filaments were higher than before exposure. This is indicative of cross-linking in each case. That cross-linking continued to be the predominating effect in some of the materials as the exposure was prolonged is indicated by the positive slopes of curves 1, 2, and 3. These curves represent the undrawn filament and the filaments drawn to ratios of 2.5:1 and 3.0:1.

The filaments drawn to a ratio of 3.5:1, although exhibiting an increase in modulus at the beginning of the exposure, decreased in modulus as the radiation was continued beyond $10^{14}$ n.v.t. or $5 \times 10^6$ R.

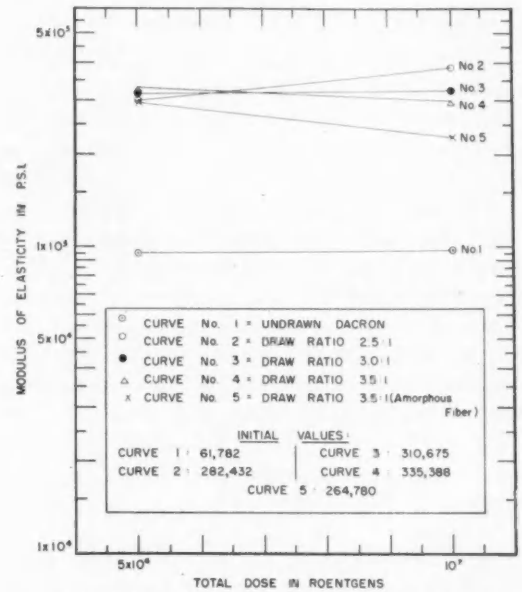
MODULUS OF ELASTICITY IN P.S.I.
TOTAL DOSE IN ROENTGENS
CURVE No. 1 = UNDRAWN DACRON
CURVE No. 2 = DRAW RATIO 2.5:1
CURVE No. 3 = DRAW RATIO 3.0:1
CURVE No. 4 = DRAW RATIO 3.5:1
CURVE No. 5 = DRAW RATIO 3.5:1 (Amorphous Fiber)
INITIAL VALUES:
CURVE 1 : 61,782
CURVE 2 : 282,432
CURVE 3 : 310,675
CURVE 4 : 335,388
CURVE 5 : 264,780

**Fig. 2.** Effect of gamma radiation on the modulus of elasticity of bright Dacron.

This was true for the filament that was crystalline (curve 4) as well as for the filament drawn in such a manner as to give an amorphous fiber (curve 5). Thus, it is concluded that, initially, some cross-linking occurs in all of the Dacron filaments but that beyond a draw ratio of 3.0:1, degradation reactions, probably chain scission, predominate over cross-linking phenomena. In Figures 3 and 4 the moduli of elasticity after exposure in the reactor and to a Cobalt-60 source are plotted as a function of draw ratio. It is evident from Figure 3, again, that above a draw ratio of three, degradation reactions predominate over cross-linking beyond a level of exposure of $10^{14}$ n.v.t. In the case of gamma irradiation alone (Figure 4), a break at a draw ratio of 2.5 is evident. In spite of this, the general conclusion that draw ratio influences the behavior of a material during exposure to high-energy radiation is valid.

The tenacities of all the filaments were significantly changed only at the highest levels of exposure, indicating that the strengths of the materials were not altered until an exposure of between $10^{16}$ and $10^{17}$ n.v.t. was reached. At the $10^{17}$ level, the tenacity had decreased about 20%. That chain scission occurs at this level was substantiated by an analysis of the filaments for carboxyl content.[4] Only the materials exposed at $10^{17}$ were different from the remaining ones in this respect. The marked rise in carboxyl content would indicate that the chain cleavage was of the hydrolytic type.

Two other observations of interest were noted. First, as indicated by curves 4 and 5 in Figures 1 and 2, there were no differences in behavior between the crystalline and the amorphous fibers of the same draw ratio, although the amorphous fiber was slightly lower in tenacity and modulus initially. Second, the same series of exposures were carried out with dull filament and the same conclusions with respect to radiation behavior were reached. The changes in tenacity and in carboxyl content percentagewise, at the highest level of exposure, were identical for the bright and dull materials.

No quantitative indication of the extent of cross-linking could be made from the present work, although it was observed that the predominance of cross-linking over degradation was greatest in the earliest stages of irradiation. It is believed that cross-linking reactions were of a low order of mag-

[4] These analyses were conducted by the Dacron Research Laboratory of E. I. du Pont de Nemours & Co., Inc.

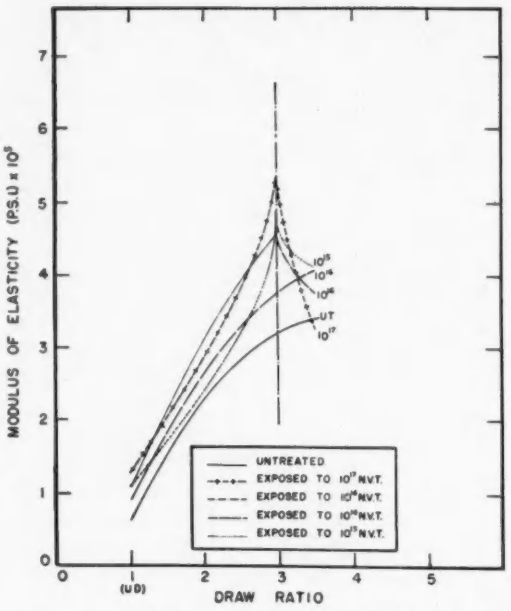


**Fig. 3.** Relation between modulus of elasticity and draw ratio for Dacron subjected to different levels of neutron radiation.

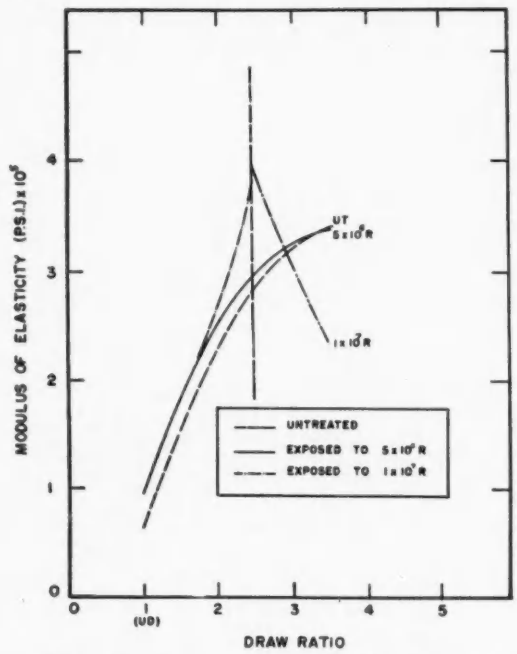


**Fig. 4.** Relation between modulus of elasticity and draw ratio for Dacron subjected to different levels of gamma radiation.

nitude because no changes in softening point were found up to and including an exposure of $10^{16}$ n.v.t. By the method used in this work, 255° C. was obtained for the untreated and the exposed materials. The melting points of the materials exposed to $10^{17}$ n.v.t. was 250° C. The solubility in m-cresol also remained practically unchanged. There was an indication that by a refined technique it could be shown that the solubility of the irradiated materials was slightly less than the untreated, but in any event, no indication of extensive cross-linking was evident.

## Conclusions

The results of the present investigation have shown that the modulus of elasticity of Dacron polyester filament may be increased by exposure to high-energy radiation. This indicated that cross-linking reactions took place and predominated over chain scission, particularly during the early stages of irradiation. Draw ratio, i.e., the degree of orientation of the filament, had an influence on the behavior. The materials of lower draw ratio tended to show more cross-linking than those of high draw ratio, the optimum being between 2.5:1 and 3.0:1. The degree of crystallinity of the filament did not influence the behavior of the filaments. Moreover, no differences were found between bright and dull filaments.

Although the work has not yet been extended to many other polymers, it is believed that materials which show a marked tendency to cross-link during exposure to high-energy radiation would show an effect similar to Dacron. For example, polyethylenes of different degrees of orientation or of different pretreatments might well behave quite differently with respect to changes in properties brought about by a given level of radiation. This has been partially substantiated by some preliminary results obtained with polyethylenes of unknown history but at the same time known to be different in character prior to irradiation.

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# Book Reviews

**The ISCC–NBS Method of Designating Colors and a Dictionary of Color Names.** National Bureau of Standards Circular 553. U.S. Department of Commerce, Washington, D. C., 1955. 158 pages. Price $2.00.

The revised Inter-Society Color Council–National Bureau of Standards color designations are defined in Munsell terms by 31 name charts, one for each of 31 ranges of Munsell hue. To form a dictionary of color names, 7,500 color names have been determined and listed both alphabetically and by ISCC–NBS color designation.

This book is an excellent attempt at clarifying the complex field of color nomenclature. In extending the designations from only opaque surfaces to other forms of matter, a useful purpose has been served.

Use of a systematized nomenclature of colors should be a welcome innovation in the textile coloring field.

**The New Sales Promotion in the Textile Industry.** James C. Cumming. Fairchild Publications, Inc., New York, 1955. 224 pages. Price $4.95.

During the past several years many new promotional techniques have been developed and employed by various organizations within the textile industry. *The New Sales Promotion in the Textile Industry* is a revision of a previous book by James Cumming. Much of the original text has been rewritten and expanded, taking into account the changes in methods and the increase in number of textile firms adopting intensive promotional campaigns.

Throughout the book, case histories of firms prominent in the industry are cited, and the reasons for the success or failure of a given campaign approach are analyzed. The pros and cons of cooperative advertising and selling the trade versus promotion at the consumer level are considered in detail.

In a chapter entitled "The Growing Importance of Television in Textile Promotion," suggestions are given on how to take advantage of the various available television techniques. By selecting the audience one wishes to reach, it is not necessarily imperative that a 50-station hook-up be bought. The textile advertiser can pick his shots. Chapters are devoted to relating how sales promotion is handled by different segments of the industry, for example, converters, men's and women's clothing manufacturers, etc.

The author is vice president and account executive for Anderson & Cairns, Inc., and has had an unusually broad experience in the advertising field. In the course of his work with the advertising agency, he was personally associated with many of the firms whose sales promotional activities he describes.

The frank presentation of the experience of successful firms makes this book an invaluable guide.

# Letters to the Editor

## The Measurement of Tearing Strength of Textile Fabrics: A Multiple Specimen Single-Rip Test

Defence Research Medical Laboratories
P. O. Box 62, Postal Station K
Toronto 12, Ontario, Canada

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

A recent paper [1] discussed the problem of interpretation of current versions of two test methods for the determination of the tearing strength of textile fabrics and suggested that the single-rip test was the more satisfactory method of those examined. It is well known, however, that the majority of fabrics, when tested by this method, exhibit tearing strength values too low to be properly determined on tensile machines commonly found in textile laboratories.

It occurred to the writer that a simple modification of the procedure might be used to overcome this difficulty. The nature of the single-rip test is such that if several test specimens were clamped in the testing machine and torn simultaneously the resultant stress measured by the machine should at any moment equal the sum of the stresses occurring in the individual test specimens (neglecting any inertia effects in the testing machine itself). In order to test this hypothesis, a number of fabrics similar to those of the group originally studied were examined by a procedure in which specimens were tested singly and in groups of two, four, or six specimens each. These fabrics were chosen merely to represent a reasonably wide range of tearing strength values. The tests were carried out on the Instron tensile testing machine, and also on the Scott Serigraph Model J-3 as a matter of interest. Thirty-six specimens were cut from each fabric according to repeats of the pattern used previously [1], and selected with the aid of random numbers for testing singly or in one of the multiple specimen tests. For each fabric 4 specimens were

**TABLE I. Tearing Strength (Single-Rip Method) in Pounds for Single and Multiple Specimens (Groups of 2, 4, and 6 Specimens)**

| (1) Fabric | (2) Testing machine | (3) Single | (4) Twofold | (5) Fourfold | (6) Sixfold | (7) Average single strength | (8) British tongue test (double-rip) |
|---|---|---|---|---|---|---|---|
| 3* | Instron | 3.85 | 7.30 | 15.05 | 22.15 | 3.72 | 6.3 |
| | Scott | 2.90 | 7.15 | 13.65 | 20.7 | 3.42 | — |
| 4* | Instron | 5.60 | 11.60 | 23.8 | 34.8 | 5.85 | 12.0 |
| | Scott | 6.50 | 13.60 | 25.4 | 36.6 | 6.3 | — |
| 5 | Instron | 5.25 | 10.75 | 21.15 | 32.65 | 5.36 | 10.3 |
| 6* | Instron | 3.80 | 7.85 | 15.80 | 23.0 | 3.88 | 7.5 |
| | Scott | 4.05 | 8.05 | 16.25 | 24.3 | 4.04 | — |
| 7* | Instron | 2.6 | 5.0 | 10.3 | 15.75 | 2.60 | — |
| | Scott | 3.25 | 6.0 | 12.0 | 17.2 | 2.95 | — |
| 10* | Instron | 2.40 | 4.60 | 9.25 | 13.60 | 2.28 | — |
| | Scott | 2.20 | 4.45 | 9.15 | 14.0 | 2.32 | — |
| 15* | Instron | 9.80 | 19.9 | 38.0 | 56.5 | 9.5 | 17.8 |
| | Scott | 10.7 | 20.25 | 37.3 | 57.4 | 9.4 | — |

* Indicates that the supply of the fabric originally used was exhausted and that a further sample, described by the same specification, was obtained for the present study.

tested singly, 8 were tested in pairs, 12 in groups of four and 12 in groups of six each. The records provided by each machine were analyzed graphically according to the procedure used previously [1] for the single specimen method, yielding the median values given in Table I.

When these data for tearing strength are plotted against the number of specimens used in the multiple specimen test, excellent linear relationships are found, which provide experimental demonstration of the validity of the multiple specimen technique. In column 7 of Table I are given the values for tearing strength of the individual fabrics represented by the slopes of the lines so drawn. It would appear that the force required to tear a group of specimens is strictly proportional to their number, and the number of specimens to be included in a multiple specimen test may therefore be chosen with reference only to the capacity of the testing machine.

As a matter of further interest, the tearing strength of each fabric was determined also by the tongue tear test (double rip) described in British Standards Handbook No. 11, [2], using the Instron testing machine. From the geometry of the test specimens, this method would be expected to give values twice those obtained by the single-rip test. The values obtained are given in column 8 of Table I and indicate that British Tongue Test values are approximately double the single-rip test values, as determined by the multiple specimen technique. Although the agreement is good, this relationship deserves more study with a larger range of fabrics. The single-rip test offers minor advantages in economy of fabric and can be carried out with the 2-in. wide jaws normally available on most testing machines.

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L. H. Turl

# The Relation between the Effective Crimp Diameter and the Fiber Diameter for Two Types of Wool Fibers

Institute for Fibers and
Forest Products Research
Ministry of Agriculture, Israel

To the Editor
Textile Research Journal

*Dear Sir:*

In previous communications [1, 2] the effective-crimp-diameter (E.C.D.) of a crimped fiber was defined as the average distance between the fiber and the straight line connecting its end points. Measurements of the E.C.D., reported there, had been carried out while the fibers were being kept under well-defined conditions of stress, which were varied by applying different loads. It has been pointed out in the previous article [2], that a higher diameter $d$ of a fiber was, in general, associated with a higher value of the E.C.D. Further observations on this relationship of the E.C.D. and the fiber diameter are reported in the present communication.

Several series of measurements have been carried out in which the E.C.D. was determined for two types of wool, i.e., 52's Scotch-Blackface and 90's

**TABLE I. Change in E.C.D. of 52's Scotch-Blackface and 90's Merino Scoured Wool Fibers with Load (w)**

| No. of fibers | Mean fiber diameter d ($\mu$) | $D_{eff}$ (mm) | | | |
|---|---|---|---|---|---|
| Load, mg | | 20 | 40 | 60 | 80 |
| 90's Merino | | | | | |
| 10 | 17.0 | 0.36 | 0.24 | 0.20 | 0.16 |
| 35 | 21.3 | 0.37 | 0.25 | 0.21 | 0.17 |
| 5 | 30.3 | 0.46 | 0.34 | 0.28 | 0.23 |
| 52's Scotch-Blackface | | | | | |
| 7 | 27.9 | 0.7 | 0.4 | 0.3 | 0.2 |
| 20 | 35.2 | 1.3 | 0.8 | 0.6 | 0.4 |
| 16 | 42.2 | 1.6 | 0.9 | 0.6 | 0.4 |
| 7 | 49.9 | 1.8 | 0.9 | 0.6 | 0.4 |

Merino wool fibers. The observed values are given in Table I in which the fibers are arranged according to increasing values of their diameter $d$. In Figure 1 and 2, the E.C.D. has been plotted for various loads as a function of the diameter of the fiber.

It is seen that the curves obtained for 52's Scotch-Blackface wool fibers under various loads differ in their general character from those obtained for the 90's Merino wool fibers: the former being convex and the latter concave toward the X axis. Although the statistical significance of this difference could not yet be conclusively established, this property of the curves seems to be stable, within the sample of fibers studied, as it is maintained in groups of fibers.

Furthermore, all the curves of the family representing E.C.D. as a function of fiber diameter for various weights, with respect to 52's Scotch-Blackface if extrapolated to small fiber diameters, seem to converge to a point situated on the X axis (i.e.,

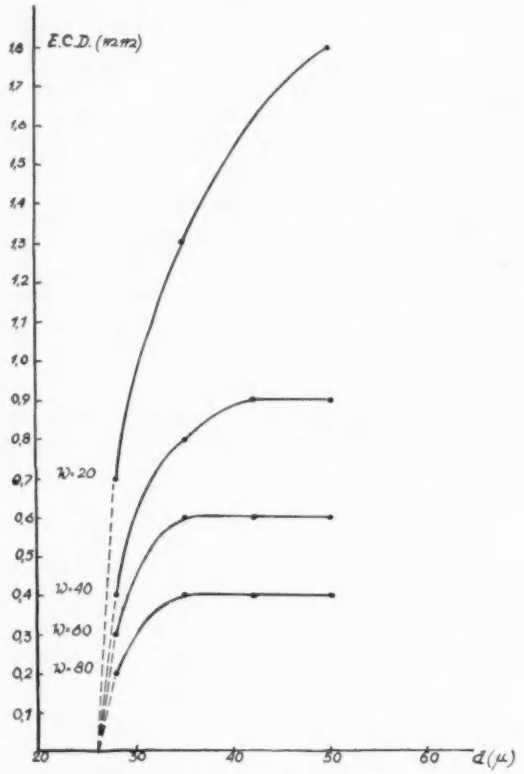


**Fig. 1.** Change in E.C.D. with diameter ($d$) of 52's fibers under different loads $w$ (mg.).

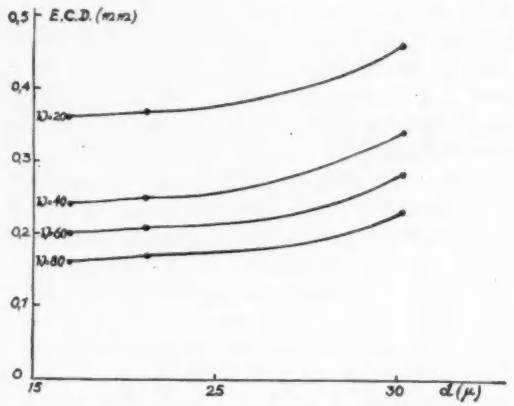


**Fig. 2.** Change in E.C.D. with diameter of 90's fibers under different loads $w$ (mg.).

E.C.D. = 0) at a fiber diameter of about 26 $\mu$. This would mean that if there existed very fine fibers of the 52's Scotch-Blackface quality, they would possess no crimp, even in the absence of any load. On the other hand, for higher fiber diameters the E.C.D. becomes almost independent of the fiber diameter, at least for the higher loads.

The corresponding family of curves for 90's Merino wool are more or less parallel and do not indicate the existence of a similar point of convergence. It would follow that even extremely fine fibers of the Merino quality should still be considerably crimped.

It thus appears that, while the E.C.D., and the effective wave number, also defined in the previous communication [2], are necessary for describing crimp of an individual fiber, the relationship between the E.C.D. and the fiber diameter seems to represent another important element for the characterization of the various types of wool fibers.

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# INDUSTRIAL SECTION

## Teflon[1] Tetrafluoroethylene Fiber[2]

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DURING the past 20 years, the textile industry has been offered a constantly increasing selection of synthetic fibers. In sheer numbers, the fibers based on acrylonitrile lead the field, especially in Europe. The polyamides have followed closely. There has been a scattering of fibers based on polyvinyl chloride and its copolymers. Only two polyesters have appeared. Among the latest, with no chemically similar companions as yet, is the Du Pont Company's "Teflon" tetrafluoroethylene fiber.

This fiber is so new that in Dr. Rowland Hill's very authoritative book entitled "Fibres from Synthetic Polymers" published in 1953, there is no clear indication that polytetrafluoroethylene is capable of being formed into a fiber at all. Nevertheless, today Teflon is available in the form of tough, highly oriented fibers possessing all the unique chemical inertness of the molded Teflon with which practically everyone in the engineering professions is familiar. It is the purpose of this paper to survey basic information concerning the properties of Teflon fiber and to outline the growing catalogue of its practical utility.

### *Molecular Structure of Teflon Fiber*

In discussing this unique fiber, it is desirable to examine first the mechanism which holds the molecules of Teflon fiber together, giving it the strength and toughness required for textile processing and for surviving the stresses and strains in the final end use.

Basically, all fiber-forming polymers consist of very long, chainlike molecules. For purposes of this discussion, it can be said that in a useful fibrous form, organic high polymers are arranged in a sort of two-phase structure, as shown in Figure 1. One phase consists of bundles of parallel molecules possessing an ordered crystalline character. These ordered bundles or crystallites are quite stiff. On the average, they are oriented parallel to the fiber axis. In the usual case, the molecules themselves are actually longer than the crystalline regions, and any given molecule may extend through several crystallites. The segments of the molecules between the crystalline regions wander randomly, crossing segments of other molecules in any direction in a formless, disordered way that gives rise to softer amorphous regions. In effect, the mechanical properties of a fiber are controlled by, first, the ratio of stiff crystalline regions to soft amorphous regions and, second, the intrinsic stiffness of the polymer molecule.

This structural picture of a fiber immediately brings up several questions when applied to Teflon tetrafluoroethylene fiber. What, for example, are the forces which bind the molecules together in the crystalline regions? Since the Teflon molecules consist of long carbon chains with all available bonds completely saturated by fluorine, the molecules are electrically neutral and there are no strong polar

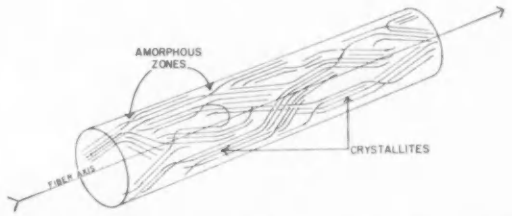


**Fig. 1.** Idealized arrangement of molecules in synthetic fiber.

[1] Registered du Pont trademark.

[2] Paper given at a joint meeting of the Commercial Chemical Development Association and the Chemical Market Research Association in Cleveland, Ohio, November 15, 1955.

forces, such as are so important in holding together the molecules of nylon, Dacron [3] polyester fiber, or the cellulosic fibers. Instead, the extreme regularity of the Teflon molecule permits very close packing of the chains, under which conditions the relatively weak, but very numerous, Van der Waals forces add up to produce substantial intermolecular attraction within the crystallites.

Next, why is the Teflon fiber soft and very flexible, yet possessed of a fairly high melting point? The answer is that the molecules are easily deformed by gross mechanical forces, and consequently, the amorphous zones in the fiber are soft. By contrast the close packing of the voluminous fluorine atoms around the carbon chain actually renders the molecules relatively immobile to forces of the order that produce Brownian movement. Consequently, the final transformation from an interlaced fibrous structure to a freely moving, molten mass does not occur until quite high levels of thermal energy are reached.

The high density Teflon fiber (2.2 g./cc.) also stems from this close packing of fluorine atoms around the carbon plus the close fitting of the molecules in the crystallites.

*Physical Properties*

With this qualitative introduction, it will be appropriate to summarize some properties of Teflon fiber in quantitative terms. This information is presented in Table I.

The comparison with a textile-type nylon and with molded Teflon resin is given to show that in the oriented fibrous form, Teflon is a true fiber possessing mechanical characteristics quite different from those of the parent resin.

*Chemical Properties*

The fact that Teflon fiber consists of nothing but carbon chains completely saturated with fluorine gives the fiber a fantastic resistance to chemical degradation. On one hand, the carbon-to-fluorine bonds are extremely strong; the only reagents that will break them are alkali metals, either molten or dissolved in liquid ammonia. On the other hand, the fluorine atoms are packed so closely around the carbon chain that the carbon-to-carbon bonds in the chain are thoroughly protected from any reagent except fluorine gas at high temperature and pressure, or by an almost equally vicious reagent, chlorine trifluoride.

Thus, Teflon fiber is completely inert to such reagents as boiling sulfuric acid, to fuming nitric acid, to aqua regia, or to boiling saturated sodium hydroxide. It is inert to all the usual powerful oxidizing reagents. Moreover, Teflon fiber has no known solvents except certain perfluorinated organic liquids at above 570° F. It will pyrolyze, losing weight at the rate of 0.0002%/hr. at 554° F., but at this temperature all the commoner natural or synthetic fibers have long since been reduced to a useless char or a pool of molten polymer.

Table II summarizes an experiment demonstrating chemical inertness of fabrics made from Teflon fiber.

*End-Use Possibilities*

The facts that Teflon fiber possessed both (1) useful mechanical properties and (2) the chemical stability of tetrafluoroethylene polymer plus a few other pertinent items were about all that was known concerning it several years ago. By that time, however, an extensive research program had resulted in a practical process for its manufacture. Accordingly, the problem was to determine what it was good for, and what sort of markets it might hope

**TABLE I. Physical Properties of Teflon Tetrafluoroethylene Fiber**

| | Oriented Teflon fiber (boiled off) | Nylon type 200 (boiled off) | Molded Teflon resin |
|---|---|---|---|
| Diameter of fiber, mils | 0.8 | | |
| Density, g./cc. | 2.2 | 1.14 | 2.2 |
| Tensile strength, p.s.i. | 50,000 | 61,000 | 2,000 |
| Elongation, % | 13 | 26 | 200 |
| Initial modulus, p.s.i. | 471,000 | 264,000 | 60,000 |

[3] Du Pont trademark.

**TABLE II. Resistance of Teflon Fabric to Hot, Corrosive Liquids**

Fabric exposed successively to:

*a.* Concen. $H_2SO_4$/554° F., 24 hr.
*b.* Concen. $HNO_3$/212° F., 24 hr.
*c.* 50% NaOH/212° F., 24 hr.
*d.* Concen. aqua regia/212° F., 24 hr.

| | Yarns per inch | | Fabric | | Yarn | |
|---|---|---|---|---|---|---|
| | Warp | Filling | Break strength, lb. | Elongation, % | Break strength, lb. | Elongation, % |
| Before | 80 | 69 | 107 | 17 | 46,500 | 15 |
| After | 88 | 80 | 111 | 19 | 39,700 | 32 |

to enter in the face of competition from existing organic fibers, from glass fibers, and from other materials such as woven stainless steel wire fabrics. From the combination of low modulus, high density, lack of easy dyeability, slick greasy tactile quality, and high initial price, it could obviously be predicted that this fiber was not going to be of any immediate interest in the general apparel market for a long time to come. It was decided that it would find its principal markets in industrial outlets and that the several pounds available should therefore be evaluated in suitable industrial end uses. But those several pounds of an experimentally produced fiber cost many thousands of dollars, and consequently could be committed only to carefully designed field tests in situations where the use of a high-priced but unique fiber such as Teflon might lead to sufficiently improved process operability or reduced equipment maintenance to warrant the increased cost.

From a preliminary end-use survey, the following list of potential applications for Teflon fiber emerged.

**TABLE III. Projected End Uses for Teflon Tetrafluoroethylene Fiber**

1. Packing for shafts on chemical pumps and valves.
2. Filtration of corrosive liquids.
3. Filtration of particles from high-temperature or corrosive gases.
4. Gasketing fabrics.
5. Laundry fabrics for press pad covers, press pads, and roll covers.
6. Sewing thread for fabrics made of Teflon.
7. Special conveyor beltings.
8. Electrical tapes and wire wraps for corrosive services.
9. Protective clothing.
10. Hose and V-belt curing tapes.
11. Special corrosion resistant cordage.
12. High density fly fishing lines.
13. Surgical uses: antistick bandages.

Obviously, the "handful" of available fibers could not be tried in all these fields. Instead, it was decided to concentrate on the first six in an effort to demonstrate whether sufficient market existed for Teflon fiber at $20.00/lb. (later reduced to $14.00/lb.), to justify its experimental manufacture on a large enough semi-works basis to support a full-fledged market development program. This question was ultimately answered in the affirmative.

*Braided Packing*

Braided packing for chemical pump shafts appeared to offer the best opportunity to demonstrate with small samples the usefulness of a fiber having a high degree of toughness plus unprecedented corrosion resistance. Its very low fiber-to-fiber coefficient of friction (0.28 dynamic, 0.20 static) also directed our thinking toward packing. Accordingly, the Garlock Packing Company was asked to make some short lengths of square, lattice braided packing which were then tested in a group of difficult packing problems with the results shown in Table IV.

In numerous other pump or valve packing tests, similar favorable results were obtained. It soon became evident that here was a truly new material for this service. With it, the packing manufacturer could assist his customer in the chemical industry in solving troublesome sealing problems in corrosive situations on pumps equipped with simple packing glands without resorting to complicated and more expensive rotary seals.

The first of the above-listed packing tests were run with a dry, braided packing. It was, however, demonstrated in the course of this investigation that the braid could be impregnated with Teflon dispersion. The lubricating and sealing action of the pasty dispersion improved the reliability of the packing. In addition, its binding action on the fibers made the packing easier to cut and shape, and it is the lubricated packing that the Garlock Company eventually put on the market as the first commercial product made from Teflon yarn.

*Filtration Fabrics*

In search of other fields to demonstrate the usefulness of Teflon fiber, tests of fabrics were set up in liquid and pneumatic filtration applications.

**TABLE IV. Packing Performance Data—Teflon Tetrafluoroethylene Fiber**

| | |
|---|---|
| Pump #1 | Labor pump handling 102% fuming nitric acid. Braided packing of Teflon fiber lasted 7 months and still in good condition. Best previous packing lasted 2 to 3 weeks. |
| Pump #2 | Centrifugal pump handling 45% $H_2SO_4$ at 170° F. Braided packing of Teflon fiber lasted 46 days. Best previous packing lasted 7 to 10 days. |
| Pump #3 | Centrifugal pump handling 40 to 78% sodium hydroxide at 330° F. Braided packing of Teflon fiber lasted 11 days. Best previous packing failed in 2 to 4 days. |
| Pump #4 | Centrifugal pump handling molten urea mixture at 130° C. Braided packing of Teflon fiber lasted 34 days. Best previous packing lasted 2 to 5 days. |

In liquid filtration as practiced with plate and frame presses, woven fabrics of Teflon performed as expected, showing no deterioration from contact with corrosive mixtures. Due to their flexibility, the fabrics sealed well around the edges of the plates. Their freedom from any tendency to adhere to the filter cake made them very easy to clean. In short, to make an ideal liquid filtration cloth from Teflon fiber, it was only necessary to choose the fabric construction.

**TABLE V. Strength of Teflon Fiber at Various Temperatures**

| Temperature* °F. | Tensile strength g.p.d. | Tensile strength p.s.i. | Modulus g.p.d. | Modulus p.s.i. | Elongation, % |
|---|---|---|---|---|---|
| −85† | 3.2 | 94,000 | 48.0 | 1,410,000 | 8.3 |
| 32† | 2.4 | 70,600 | 34.0 | 1,000,000 | 9.0 |
| 70† | 1.3 | 38,200 | 14.0 | 412,000 | 12.0 |
| 70‡ | 1.6 | 47,000 | 15.0 | 442,000 | 15.0 |
| 70§ | 1.6 | 47,000 | 16.0 | 471,000 | 13.0 |
| 100 | 1.1 | 32,300 | 12.0 | 354,000 | 14.0 |
| 150 | 0.8 | 23,500 | 9.0 | 265,000 | 16.0 |
| 200 | 0.6 | 17,700 | 7.4 | 217,000 | 14.5 |
| 300 | 0.4 | 11,800 | 4.9 | 144,000 | 7.8 |
| 400 | 0.3 | 8,800 | 3.8 | 112,000 | 7.0 |
| 450 | 0.2 | 5,900 | 2.9 | 85,400 | 7.4 |
| 500 | 0.2 | 5,900 | 2.5 | 73,500 | 7.0 |
| 550 | 0.2 | 5,900 | 2.5 | 73,500 | 7.0 |

* In air except where indicated.
† In hexane.
‡ Wet.
§ 65% R.H.

**TABLE VI. High Temperature Properties of Fabric of Teflon**

| Temperature, °F. | Warp tensile strength, lb./in. | Warp elongation, % |
|---|---|---|
| 70 | 61 | 16 |
| 200 | 33 | 19 |
| 300 | 19 | 16 |
| 450 | 12 | 20 |
| 500 | 12 | 23 |
| 600 | 9 | 44 |

For the filtration of particles from hot, corrosive gases, fabrics of Teflon fiber have been found to be extremely useful. Here the problem is more complex. As yet, no gaseous filtration task has been encountered in which the fabric is jeopardized by corrosive materials in the gas stream. However, the temperatures involved in some gaseous filtrations are sufficiently high to reduce the strength of the fiber. This makes it necessary to guard against excessive tensile stresses and abrasion in services at elevated temperature.

In this regard, it is of interest to consider quantitatively what does happen to the tensile properties of Teflon fiber as the temperature varies. The available data are summarized in Table V.

Fabric strengths follow a similar pattern, as shown in Table VI.

While the data in Tables V and VI shows that both Teflon fiber and fabric soften at elevated temperature, they also show that there is still adequate strength available for some applications at 500° F.—a temperature where most commercial fibers are essentially useless.

*Thermal Stability*

Another factor which must be included in any examination of the high-temperature characteristics of Teflon fiber or fabric is the way in which they resist long-term exposure to elevated temperature. The following table summarizes representative data on the fiber.

Table VII covers two aspects of the fiber's high-temperature behavior. It demonstrates first, that the fiber can, to a reasonable degree, stand severe thermal shock, namely, the 1 min. at 600° F. However, this temperature is above the recommended maximum service temperature for Teflon since the fiber begins to undergo slow pyrolysis and gives off toxic gaseous decomposition products.

A fairer statement of the high temperature durability of Teflon fiber is contained in the lower three

**TABLE VII. Effect of Extended Exposure at High Temperature on Physical Properties of Teflon Fiber**

(All properties measured at room temperature)

| Exposure conditions | Denier | Tenacity, g./d. | Elongation, % | Modulus, g./d. | Toughness (ten.×elong.) | Shrinkage, % |
|---|---|---|---|---|---|---|
| Before exposure | 410 | 1.68 | 15 | 15 | 25 | — |
| After 1 min. @ 600° F. | 455 | 1.42 | 20 | 4.2 | 28 | 7 |
| After 2 hr. @ 500° F. | 456 | 1.37 | 25 | 4.3 | 34 | 9 |
| After 24 hr. @ 500° F. | 463 | 1.39 | 27 | 3.3 | 38 | 12 |
| After 8 days @ 500° F. | 462 | 1.38 | 26 | 4.6 | 26 | 12 |

**TABLE VIII. Heat Shrinkage of Fabric of Teflon Fiber**

| Time of exposure | % Accumulated shrinkage when exposed to | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 275° F. | | 400° F. | | 500° F. | | 600° F. | |
| | Warp | Filling | Warp | Filling | Warp | Filling | Warp | Filling |
| 1 min. | 0 | 0 | 0.2 | 0.4 | 3.7 | 3.8 | 11.1 | 12.6 |
| 5 min. | 0 | 0 | 1.6 | 1.3 | 4.3 | 4.4 | | |
| 30 min. | 0.2 | 0.4 | 1.9 | 1.7 | 6.1 | 5.9 | | |
| 2 hr. | 0.3 | 0.6 | 3.0 | 3.0 | 7.9 | 7.9 | | |
| 96 hr. | 0.7 | 1.1 | 6.3 | 6.2 | 10.2 | 10.4 | | |
| 192 hr. | 1.3 | 2.0 | 7.3 | 7.6 | 10.5 | 10.6 | | |
| 384 hr. | — | — | 7.6 | 7.6 | 10.7 | 10.8 | | |

lines of Table VII. The data show that after an initial shrinkage amounting to 12%, accompanied by an increase in denier and a decrease in modulus, the fiber stabilized at about 1.38 g./den. tenacity and remained at that level for 8 days. Actually, the tenacity and elongation product or toughness of the fiber did not change a great deal from its original value, indicating as one might expect that the fiber's chemistry was not being seriously affected by the 500° F. temperature.

*Heat Setting Fabric of Teflon Fiber*

From a practical viewpoint, these data suggest that fabrics of Teflon fiber can be "heat set" to prevent sudden or progressive shrinkage in service. This is quite possible if the correct conditions are used. Tables VIII and IX demonstrate what is required.

Note that at 400° F. the fabrics apparently began to stabilize after 96 hr. exposure in the sense that the accumulated shrinkage did not change. To determine whether or not it was possible to eliminate the tendency toward thermal shrinkage entirely, fabric was exposed completely relaxed to 600° F. air for 1 min. Thereafter, when it was exposed to 400 or 500° F. air, progressive shrinkage was significantly reduced, as shown in Table IX.

Obviously for complete stabilization the time of the 600° F. treatment might be increased. A more satisfactory procedure is to remove major shrinkage by the 600° F. tension-free treatment in hot air and thereafter to allow for the small amount of shrinkage which will occur during further exposure at the lower temperatures.

Attempts to stabilize fabric of Teflon fiber by high temperature treatment under tension or by partial shrinkage to predetermined dimensions have not proved successful.

**TABLE IX. Service Temperature Shrinkage of Preshrunk Fabric of Teflon Fiber**

(Fabric preshrunk relaxed in 600° F. air for 1 min.)

| Time of exposure, hr. | % Accumulative shrinkage when exposed to | | | |
|---|---|---|---|---|
| | 400° F. | | 500° F. | |
| | Warp | Filling | Warp | Filling |
| 48 | 0.2 | 1.0 | 2.6 | 3.0 |
| 96 | 0.6 | 1.4 | 3.1 | 4.1 |
| 192 | 1.1 | 2.2 | 3.2 | 4.2 |
| 384 | 1.1 | 2.5 | 3.5 | 4.2 |

On the basis of the foregoing information concerning the effect of elevated temperatures on Teflon fabric, it is apparent that fabrics of Teflon fiber can be used at temperatures above 400° F. and in certain cases at temperatures as high as 500° F.

*Gasketing Materials—Fabrics and Felts*

Teflon fiber has a combination of chemical resistance, and softness, coupled with mechanical toughness considerably in excess of that possessed by the massive polymer. These properties strongly suggested that it would be of interest as a gasketing material for pipe flanges handling corrosive liquids provided it could be fabricated into a suitably resilient structure. Early trials with heavy fabrics either dry or impregnated with a dispersion of Teflon showed the woven fabric gaskets to be merely equivalent to solid, and less expensive, sheeting of Teflon, in ability to produce seals at pipe flanges. Relatively high flange pressures were required and the margin of safety between the sealing pressure and the pressure at which the gasket would fail under compression was not very wide.

However, in the course of this work, gaskets consisting of Teflon fiber felts plus Teflon dispersion

**TABLE X. Sealing Pressure Required for Gaskets of Various Materials**

(Pressure shown is that required to seal off an air leak at bottom of a 0.010-in. deep depression on flat flange)

| Gasket material | Pressure required for seal, p.s.i. |
|---|---|
| Teflon felt impregnated with Teflon resin | 900 |
| Soft rubber | 1,250 |
| Solid Teflon | 7,500 |
| Asbestos composition | 10,000 |

were developed. These gaskets were quite easily compressed and accordingly exhibited an unusual ability to produce tight seals of low flange pressures. This made them useful for sealing the flanges on glass pipelines where the relatively fragile flanges prohibit the use of high flange pressures. A comparison of the sealing pressures required for impregnated Teflon felt gaskets and other commonly used materials is given in Table X.

On the basis of the above data, gaskets of Teflon impregnated Teflon felts are strongly recommended for sealing the flanges of glass or other fragile piping. In one case a system consisting of a glass-lined heat exchanger plus glass-lined piping handling 99.3% $H_2SO_4$ at 200° C. and 14 p.s.i.g. has been operating satisfactorily for five months. The previously used molded gaskets consistently failed by extrusion in less than a week, frequently with expensive consequences. As a result of the above-cited performance, maintenance engineers in charge of this equipment have started a much broader program of use and evaluation of the impregnated Teflon felt gaskets. This new gasketing material is now being made by the Fabrics and Finishes Department of the E. I. du Pont Company.[4]

In addition, the same department is making unimpregnated Teflon felts. These are finding use in filtration of highly corrosive liquids, in the removal of suspended particles from hot corrosive gases, and in the filtration of liquid fuels and lubricants at high temperatures. Felts of Teflon fiber are also finding use in the solution of high temperature lubrication problems in sealed systems. The following table summarizes the physical properties of representative specimens.

[4] Detailed information on price, performance, and availability can be obtained from that department.

**TABLE XI. Physical Properties of Felts of Teflon Fiber**

| | | | |
|---|---|---|---|
| Nominal thickness, mils | 63 | 125 | 250 |
| Weight, oz./sq. yd. | 17 | 45 | 125 |
| Tensile strength, p.s.i. | 800 | 1100 | 1800 |
| Elongation, per cent | 100 | 100 | 125 |
| Bursting strength, lb.* | 220 | 250+ | 250+ |
| Gurley porosity, sec.† | 1.6 | 4.7 | 12.0 |

* Ball Method, ASTM D-231-46.

† Seconds required for passage of 100 cc. of air through 1/10 sq. in. area.

*Sewing Thread*

Sewing thread was an item that became of some importance early, since wherever the corrosion and thermal resistance of fabrics of Teflon were of interest, it was necessary to sew the end use article with a thread of equal durability. In experimental fabrication of sewing threads for early end-use tests, no particular difficulty was encountered in achieving a balanced thread capable of running smoothly on a standard sewing machine. By now the Premier Thread Co. has experimented with thread of Teflon fiber sufficiently to have established standard constructions which they are offering for sale.

*General Textile Processing Considerations*

A large portion of Teflon yarn sold today is in the form of continuous filament 400-den. 60-filament yarn having 1 turn/in. twist. A 1200-den. 180-filament 1-turn twist yarn is also available as are uncrimped staple and tow (6.6 den./filament).

In processing the low twist continuous filament yarns through plying, twisting, spooling, warping and weaving, it is highly desirable to use a suitable sizing agent. A 2% coating of a polyvinyl alcohol resin such as Du Pont's "Elvanol" 72–60 has proven useful in this regard. It keeps the filaments together during quilling, warping, or weaving and can be readily removed later by scouring the fabric.

Plied filament yarns or sufficiently twisted (7–15 t.p.i.) single end yarns can be processed without sizing.

Where it is necessary to tie two continuous filament yarns together, use of the double weaver's knot is recommended.

In some cases, it has been desirable to make spun yarn from Teflon fiber, especially for protective garments where the slick, waxy feel of continuous filament Teflon fiber is unpleasant. However, processing a low friction fiber such as Teflon fiber into spun staple yarns is more difficult than is the case

with most other synthetic fibers. Card webs and sliver tend to fall apart under their own weight. The low mass cohesion of the filaments can to some extent be overcome by blending in 3% of rayon staple. Powdering with rosin helps. Addition of small quantities of asbestos has also aided carding and spinning.

Recently it has been found possible to make very satisfactory spun yarns by using the direct spinner. This system eliminates the troublesome carding step entirely by randomly breaking the filaments in a heavy continuous filament, low twist, yarn, immediately drawing down to the required size, and then twisting the fibers into a spun staple yarn. Excellent yarn uniformity has been achieved and the resulting fabrics have a much less waxy feel than fabrics from comparable weight Teflon continuous filament yarn. Where a more uniform, highly porous, yet dimensionally stable fabric is desired, "Taslan" [5] textured yarn of Teflon can also produce fabrics having a dry, spun-type hand without resorting to conventional spinning systems.

*Finishing and Bleaching*

Finishing techniques for Teflon fabrics must be developed to suit the individual fabric and with due consideration being given to the end use for which the fabric is designed.

One interesting finishing step that has been demonstrated in the laboratory but not yet been applied commercially is bleaching of Teflon fabric. The preferred method for obtaining the best white is to expose the yarn or fabric to a mixture of concentrated sulfuric and nitric acids. The rate of bleaching is dependent on temperature. At 600° F. it takes only a few minutes, while at 250° F. it takes several hours. A convenient technique has been to place the sample in boiling sulfuric while intermittently adding small portions of nitric acid through a dropping funnel reaching to the bottom of the vessel. Physical properties of bleached yarn are closely equivalent to those of the heat relaxed, unbleached yarn.

[5] Du Pont trademark.

## Summary

In summarizing the outlook for Teflon fiber today, it can be predicted safely that the high price will certainly limit its use to those textile problems which can be solved by no other fiber. However, its filamentary form permits Teflon to be processed into fabrics, fibrous sheeting, and felts not possible with conventional molding resins. Because of its exceptional corrosion resistance, it can be used under conditions which no other organic fiber can endure. Consequently, where the chemical or thermal environments are sufficiently rigorous to warrant its use, there is mounting evidence that Teflon tetrafluoroethylene fiber presents a new material of construction that can rapidly become an important auxiliary tool to the chemical industry.

## Acknowledgments

The writers gratefully acknowledge the contributions of a number of their colleagues who have at various times been actively associated with the product development work on "Teflon" fiber. This acknowledgment especially includes W. R. Schmidt, J. A. Piccard, G. L. Moler, B. S. Farquhar, R. A. Buckley, C. Boyer, R. J. Covell, R. Woodell, J. R. Emery, H. R. Krysiak, H. P. Von Bucher and J. W. Hannell, Jr.

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# The Effects of Fiber Fineness (Micronaire) on the Weaving Contraction in Selected Cotton Fabrics

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## Introduction

Weaving contraction, as the term is used in this paper, may be defined as the decrease in length and/or width when comparing the grey fabric dimensions, after removal from the loom, with the yarn dimensions as measured in the loom. This decrease in length and/or width is the result of the yarn axes being forced to describe a series of curves along the plane of the fabric due to the interlacing of the yarns, which takes place at the time of the beating-up and shedding motions during weaving. The amount of this contraction in weaving is influenced by yarn diameters, yarn density, yarn flexibility, warp and filling tensions, and fabric construction. Due to the differences in yarn structure, yarn preparation, and weaving tensions, the amount of contraction will not usually be the same for warp and filling, even in square constructions, i.e., when the warp and filling are of the same yarn number and there are the same number of ends and picks per square inch.

It has been shown that many yarn characteristics are influenced by fiber fineness; therefore, it follows that weaving contraction would probably be influenced by fiber fineness. Although extensive work has been done on the geometric structure of fabrics and yarns [1 through 10], little data have been reported on this particular aspect of fabric structure. Peirce [8], in his excellent geometric analysis of fabric structure, suggested that differences in fiber "hair weight per centimeter" was a concomitant factor in yarn structure; however, the consideration of the effects of fiber fineness on yarn structure was beyond the scope of that particular study. Barella [1] and Schwarz [9] considered the importance of twist and fiber packing in yarn structure, and Hoffman [3] considered the bulkiness of yarns resulting from the use of fibers of mixed diameters. In none of the above studies, however, did the authors consider the relationship between yarn structure and the differences in fiber fineness which are a result of differences in degree of cell-wall development. Since cotton fibers are uniform neither in geometric shape nor in cross-sectional area, the difficulties encountered in predicting cotton yarn structure on the basis of fiber properties are increased.

In previous experiments in the ACCO Laboratory, involving woven fabrics, it had been observed that the amount of weaving contraction varied when cottons with different Micronaire readings were used. No definite relationship had been established, however, nor was it certain that these variations in contraction could be attributed directly to fiber fineness (Micronaire). The purpose of this study was, therefore, to investigate, by experimentation, one aspect of this contraction—the influence of fiber fineness on the ultimate weaving contraction in selected fabrics.

The samples used in this study were processed using conventional methods, and the fiber and yarn tests were made using standard methods. The yarn number and twist of the filling yarns were controlled carefully, many of the spinning cycles being repeated several times in order to bring these two factors within the desired tolerances.

By using multiple, partial, and simple correlation analyses, studies were made of the effects of fiber fineness, twist, and staple length upon the percentage of weaving contraction in a 44 × 42 coarse sheeting fabric, using 20's warp and 15.7's filling. Additional tests were made, using a 34 × 32 Osnaburg fabric with 14's warp yarns and various filling yarns.

A related study was also made of the differences in effective yarn diameter resulting from various degrees of cell-wall development as measured with the Micronaire.

## Procedures

### *Coarse Sheeting*

A total of ten three-bale blends was spun for this part of the study. The grades and fiber properties of these blends are shown in Table I.

The first blend (Strict Low Middling Lt. Sp. $\frac{7}{8}$ in.) had a Micronaire reading of 2.5 and was included to compare the effects of an extremely fine, short cotton with those of other, more nearly average cottons.

A 30-lb. sample from each blend was processed, maintaining the same conditions for each test, and using, as nearly as practicable, the same machine speeds and settings. It was necessary, however, to alter the speeds and settings occasionally to compensate for the wide ranges in Micronaire reading and fiber length. Five sets of filling yarns, each set having a different twist, were spun from each of the ten blends (50 filling samples), the spinning draft and twist being changed as necessary to produce the desired actual twist and yarn number. Twist multipliers of 3.20, 3.40, 3.60, 3.80, and 4.00 were used.

The warp used in this part of the study had been made previously from 20's yarn, spun from Middling light spotted 15/16-in. cotton with a Micronaire reading of 3.4. This same warp was used in all tests, since to produce ten separate warps would have exposed the study to additional possible variations; furthermore, since the warp yarn was maintained constant, any change in warp contraction would be a function of inherent changes in filling structure or the result of a condition similar to Peirce's "crimp interchange" [7, 8], i.e., a shifting of crimp from filling to warp or from warp to filling, due to changing tensions or stresses being applied to the fabric. (Peirce's studies were made by alternately applying stresses to the fabric, after it had been removed from the loom, in the warp and filling directions, and thereby shifting the residual crimp from one direction to the other. Altering the warp and filling tensions in the loom will cause a similar redistribution of the crimp when comparing one fabric with another.)

**TABLE I**

| Class | | Length (Fibrograph, upper half mean, in.) | Fiber strength (Pressley, 1000 lb./sq. in.) | Fiber fineness (Micronaire reading) |
|---|---|---|---|---|
| Grade | Staple length (in.) | | | |
| SLM Lt. Sp. | $\frac{7}{8}$ | 0.93 | 73 | 2.5 |
| M | $1\frac{1}{16}$ | 1.06 | 82 | 3.0 |
| M | $1\frac{1}{16}$ | 1.09 | 86 | 4.1 |
| M | $1\frac{1}{16}$ | 1.09 | 86 | 5.1 |
| M Lt. Sp. | 1 | 1.04 | 80 | 3.2 |
| M Lt. Sp. | 1 | 1.03 | 81 | 4.4 |
| M Lt. Sp. | 1 | 1.06 | 76 | 5.4 |
| SLM | $\frac{29}{32}$ | 0.92 | 75 | 3.0 |
| SLM | $\frac{29}{32}$ | 0.85 | 83 | 4.3 |
| SLM | $\frac{29}{32}$ | 0.88 | 84 | 5.1 |

The percentage of warp contraction was determined by marking the warp yarns in the loom at intervals of 60 cm., and as each mark reached the fell of the fabric, a colored pick was inserted. This procedure was repeated until six "bands" of fabric were woven from each of the 50 filling yarns. In weaving the fabric test samples, the 50 bobbins of filling yarn (10 blends, 5 twist multipliers each) were marked and placed in a box from which they were selected at random. This was done to thwart any trend which might have developed as a result of progressing gradually from fine to coarse cottons, as well as the possible influence of any periodicity of variations in warp tension [6]. When the fabric was removed from the loom, the distances between the colored picks were measured and the percentage of warp contraction thereby determined. The percentage of filling contraction was determined by measuring the width of the warp ends in the reed and then the fabric width upon removal from the loom.

Since the warp ends were under loom tension at the time of the original markings, a number of ends were marked, using the method described above, and removed from the loom at intervals during the weaving phase of the study, in an effort to determine the magnitude of the possible influence of warp tension. Measurement of these ends showed no significant change in length when not under tension.

The length and width of each fabric specimen were measured after removal from the loom, and the exact locations of the measurements were marked in order that duplicate readings could be made the following day. It was found that the fabric continued to contract for approximately 48 hr. after removal from the loom. For that reason, the readings used in this study were obtained on the third and fourth days after removal from the loom. The weaving contraction data shown in Figures 1, 2, and 3 were obtained by using the means of the five length and five width measurements made on each sample.

The differences in the percentages of warp contraction when using filling yarns made from cottons of different finenesses were not consistent. It is interesting to note, however (Figure 1), that although the 29/32-in. staple and the 1-in. staple samples

showed their largest amounts of warp contraction in the 4.1 to 4.4 Micronaire range, this was countered by a lower than expected filling contraction in the same samples (Figure 2), and the area contraction (Figure 3) showed a continued decrease as the coarser cottons were used. This indicates a certain amount of "crimp interchange" between warp and filling which was observed to occur at random throughout the study.

The trend of a decrease in the amount of area weaving contraction as the coarser cottons were used is substantiated by the results of the correlation analyses, which showed an inverse relationship ($b_{13\cdot24} = -0.429$) between weaving contraction and Micronaire readings. The coefficient of multiple linear correlation for this relationship was 0.805. In making these correlation analyses, the percentage of area weaving contraction was taken as the dependent variable, because, as stated previously, a change in warp contraction, the warp yarn being constant, would be a function of filling change and/or "crimp interchange." The Micronaire reading, twist of the filling yarn, and the staple length were the independent variables. Collectively, fiber fineness, staple length, and twist accounted for approximately two-thirds of the variance in the amount of weaving contraction, with a coefficient of multiple linear correlation of 0.830 (Table II). The influence of these three factors on the amount of weaving contraction in the fabric rank in descending order of importance as follows:

1. Micronaire reading
2. Staple length
3. Twist (T.P.I.)

The relationships between staple length and percentage of area weaving contraction are shown in Figure 4. This figure shows a slight increase in the percentage of area weaving contraction with an increase in staple length; the partial correlation coefficient for this relationship was 0.660. The vertical spread in Figure 4 is the result of differences in Micronaire readings. The partial correlation coefficient between twist and the percentage of contraction (within the range of twist studied) was only 0.235, indicating that the amount of twist did not have a significant effect on the percentage of area weaving contraction.

Replicate series of filling yarns were spun from the same blends and woven into a fabric of the same construction. These filling yarns were approximately the same count as those spun during the first test. Only width measurements were made on this fabric and from these measurements and the width in the reed, the percentages of filling contraction were determined. There was good agreement between the first and second tests, insofar as the relationship between Micronaire reading and the percentage of filling contraction is concerned (Figure 5).

*Osnaburg*

In order to obtain further data, seven cottons with Micronaire readings ranging from below scale to 6.2

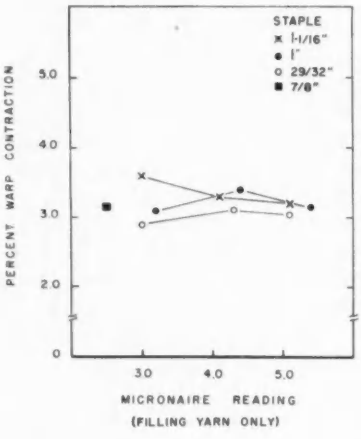



**Fig. 1.** Warp contraction, fiber fineness, and staple length (coarse sheeting).

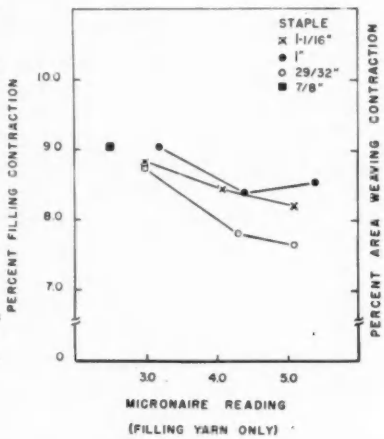



**Fig. 2.** Filling contraction, fiber fineness, and staple length (coarse sheeting).

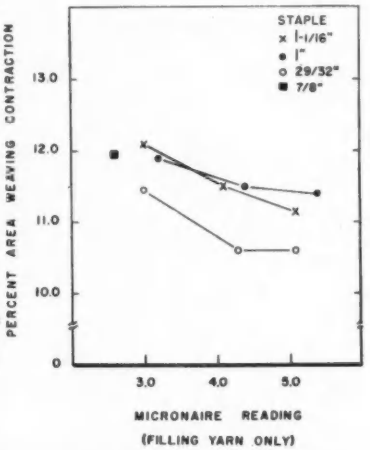



**Fig. 3.** Area contraction, fiber fineness, and staple length (coarse sheeting).

**TABLE II. Results of Correlation Analyses of the Relationship between Weaving Contraction and Fineness Micronaire, Staple Length, and Twist**

(Coarse sheeting, first test)

Variables used

Dependent: 1. Percentage of area weaving contraction
2. Twist (T.P.I.)

Independent: 3. Micronaire reading
4. Staple length

| | | $r^2$ | $r$ |
|---|---|---|---|
| Simple correlation | | | |
| Micronaire reading | | 43.1 | 0.656 |
| Staple length | | 9.9 | 0.315 |
| Twist (T.P.I.) | | 0.9 | 0.095 |
| Multiple correlation, two independent variables | | $R^2$ | $R$ |
| Micronaire reading–staple length | ($R_{1.34}$) | 66.8 | 0.817 |
| Micronaire reading–twist | ($R_{1.23}$) | 44.5 | 0.667 |
| Twist–staple length | ($R_{1.24}$) | 11.0 | 0.322 |
| Multiple correlation, three independent variables | | $R^2$ | $R$ |
| Micronaire–staple length–twist | ($R_{1.234}$) | 68.6 | 0.828 |
| Partial correlation, two independent variables | | $r^2$ | $r$ |
| Micronaire reading–staple length constant | ($r_{13.4}$) | 63.2 | 0.795 |
| Micronaire reading–twist constant | ($r_{13.2}$) | 44.0 | 0.664 |
| Staple length–micronaire reading constant | ($r_{14.3}$) | 41.7 | 0.646 |
| Staple length–twist constant | ($r_{14.2}$) | 10.1 | 0.318 |
| Twist–micronaire reading constant | ($r_{12.3}$) | 2.5 | 0.158 |
| Twist–staple length constant | ($r_{12.4}$) | 1.2 | 0.110 |
| Partial correlation, three independent variables | | $r^2$ | $r$ |
| Micronaire reading–staple length–twist constant | ($r_{13.24}$) | 64.7 | 0.805 |
| Staple length–micronaire reading–twist constant | ($r_{14.23}$) | 43.5 | 0.660 |
| Twist–micronaire reading–staple length constant | ($r_{12.34}$) | 5.5 | 0.235 |

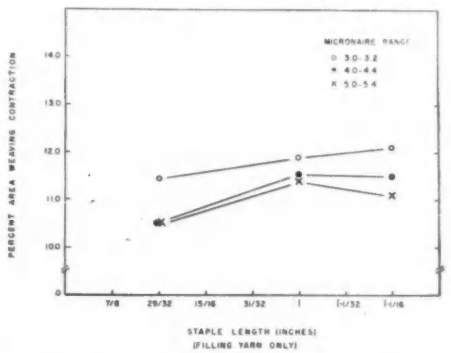



**Fig. 4.** Staple lengths of cottons used in filling yarns and the percentage of area weaving contraction in a coarse sheeting fabric.

**TABLE III**

| Grade | Class: Staple length (in.) | Length (Fibrograph, upper half mean, in.) | Fiber strength (Pressley, 1000 lb./sq. in.) | Fiber fineness (Micronaire reading) |
|---|---|---|---|---|
| MT | 7/8 | 0.86 | 67 | B.S.* |
| MYS | 7/8 | 0.94 | 65 | 2.6 |
| SLM | 29/32 | 0.94 | 81 | 3.1 |
| SLM | 29/32 | 0.86 | 84 | 4.3 |
| SLM Lt. Sp. | 29/32 | 0.96 | 79 | 4.8 |
| SM Lt. Sp. | 29/32 | 0.96 | 88 | 5.2 |
| SM Lt. Sp. | 29/32 | 0.87 | 84 | 6.2 |

* Below 2.4 on the Micronaire scale.

were selected for spinning filling yarns to be used in a 34 × 42 Osnaburg fabric. The grades and fiber properties of these samples are shown in Table III. Samples of 9's and 12's filling were spun from each of these seven cottons, using only one twist multiplier since it had already been found that within the range studied, twist was of little consequence. The yarn number and twist of these yarns were controlled carefully, as they had been for the sheeting tests.

Following the same marking procedure as was used in the sheeting fabrics, three fabric specimens were woven from each of the fourteen filling samples, using a 14's warp spun from ¾-in. staple cotton. Between each set of specimens, a section of surplus fabric was woven, using the two adjacent fillings, in order that any change in width would occur in a part of the fabric that would not be used for meas-

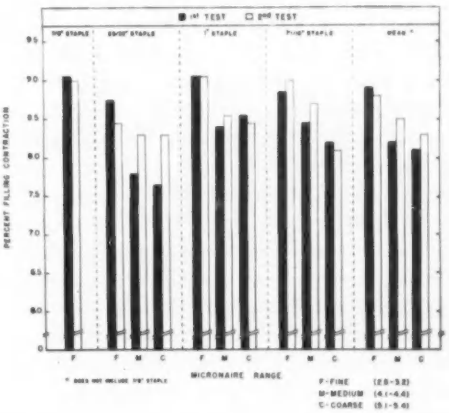



**Fig. 5.** Comparison of the percentages of filling contraction obtained in coarse sheeting when using fine, medium, and coarse cottons.

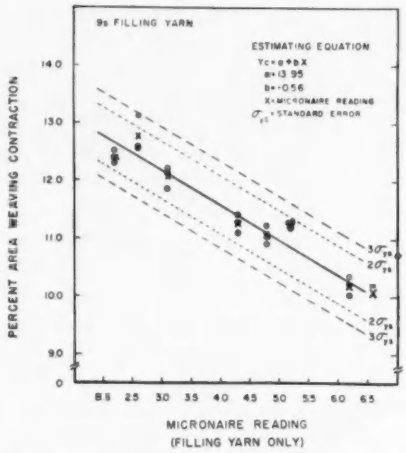



**Fig. 6.** Micronaire readings of cottons used in 9's filling and the percentage of area weaving contraction, with the regression equation for estimating the area weaving contraction for given Micronaire readings.

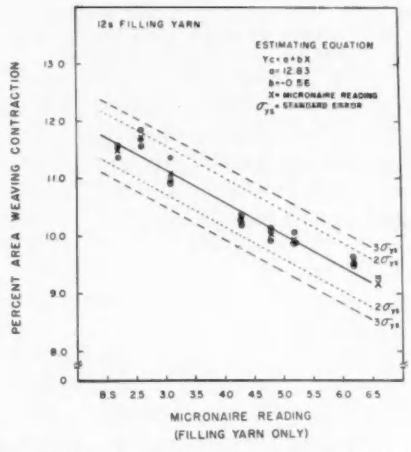



**Fig. 7.** Micronaire readings of cottons used in 12's filling and the percentage of area weaving contraction, with the regression equation for estimating the area weaving contraction for given Micronaire readings.

uring. The data obtained from these tests show the same trend as did the sheeting tests, i.e., a decrease in the amount of contraction when coarser cottons were used. It will also be noted that the 12's filling caused less contraction than did the 9's filling, as expected (Figures 6 and 7).

The equations for estimating the percentage of area weaving contraction are in Figure 6 and Figure 7 for the 9's and 12's filling, respectively. These equations were obtained from a simple linear correlation analysis of the relationship between the Micronaire readings and the percentages of area weaving contraction. The circles represent the means of the individual specimens, whereas the $X$'s are the grand means. With only two exceptions, the individual specimens fell within two times the standard error of the estimate. The simple correlation analyses of these data show a correlation coefficient between the Micronaire reading and the percentage of area weaving contraction of 0.955 for the 9's filling and 0.965 for the 12's filling.

It was theorized that the changes in the amount of weaving contraction were the result of either different fiber packing characteristics or different yarn diameters. For this reason, a basis of comparison between the changes due to variations in a yarn characteristic of known value was sought. In order to provide such a basis, samples of the two cottons with Micronaire readings of 3.1 and 6.2 were selected for spinning seven sets of filling yarns ranging from 8's through 14's in increments of one yarn number. The spinning of these yarns was controlled carefully to induce approximately the same twist angle in each yarn and to produce yarns of the desired count. These filling yarns were woven into the Osnaburg warp to determine the amount of change in weaving contraction resulting from the various yarn numbers, i.e., the effect of filling yarn diameter on weaving contraction.

Three fabric specimens were woven, using the same procedure as in the first Osnaburg test. The percentages of warp, filling, and area weaving contraction were again determined from 18 measurements made on each sample. The percentages of area weaving contraction decreased consistently with a decrease in yarn diameter (Figure 8). The percentages of warp contraction decreased with yarn diameter in terms of increasing yarn numbers (Figure 9). The yarn numbers shown in these figures were plotted according to decreasing yarn diameter, as described by Peirce's formula

$$d = 36\frac{1}{\sqrt{N}}$$

Where:

$d$ = yarn diameter in 1/1000 in.

$N$ = yarn number

It can be seen by comparing Figures 3, 6, 7, and 8 that the trend of the change in contraction is quite

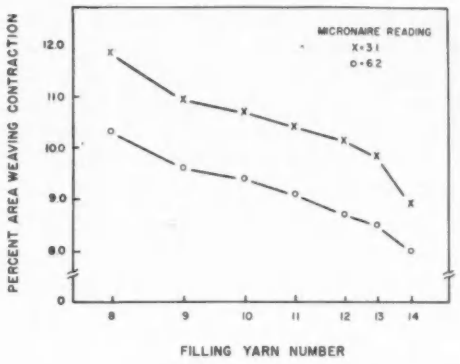



**Fig. 8.** Yarn numbers and percentage of area weaving contraction for fine and coarse cotton (Osnaburg).

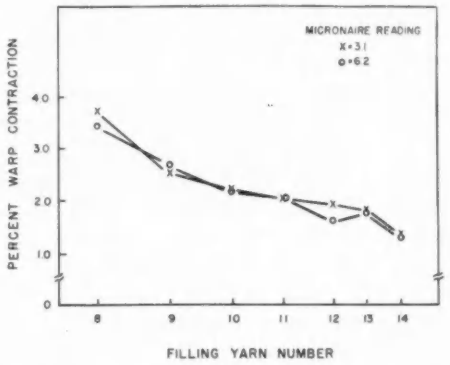



**Fig. 9.** Yarn numbers and percentage warp contraction for fine and coarse cotton (Osnaburg).

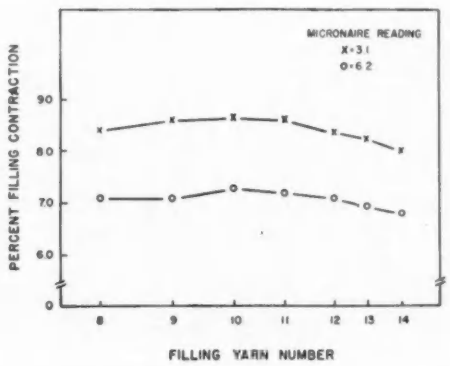



**Fig. 10.** Yarn numbers and percentage filling contraction for fine and coarse cotton (Osnaburg).

similar when using the same counts spun from cottons with various Micronaire readings or various counts spun from cottons with the same Micronaire readings.

It is interesting to note, however, from the data shown in Figures 9 and 10, that the most consistent change in the amount of weaving contraction occurred in the warp yarns, with the amount of filling contraction for each cotton remaining approximately the same regardless of yarn number. This is opposite to what occurred in the previous tests and is attributed to the lessened warp tension necessary to weave such a wide range of filling yarns, which permitted a condition similar to what Peirce describes as "crimp interchange." This did not, however, affect the ultimate over-all result which shows a decrease in the percentage of area weaving contraction as the finer fillings were woven (see Figure 8).

*Yarn Diameter*

The changes in weaving contraction resulting from variations in Micronaire reading when the same counts were spun, therefore, appeared to be a function of yarn diameter, the cottons with the lower Micronaire readings producing yarns with a larger effective diameter. In order to investigate this yarn characteristic, the following study was made.

Samples of the Middling $1\frac{1}{16}$-in. cotton with Micronaire readings of 3.0 and 5.1 were processed into 1.50 H.R., the roving weights being controlled carefully. When 300 m. of roving had been produced from each sample, the diameters of the bobbins were measured and compared. It was found that the bobbins produced from the cotton with a 3.0 Micronaire reading were approximately $\frac{1}{4}$ in. larger in diameter than those made from the cotton with a 5.1 Micronaire reading. The two sets of roving were then placed on directly opposite sides of the spinning frame in order that the spindles used in spinning would be driven by the same tapes, and were spun into 14's yarn. Under these conditions, it was also possible to control accurately the yarn number and actual twist, since the frame was equipped with a twist gear for each side. The spinning was continued until the travelers began rubbing the yarn on the bobbins using the cotton with a 3.0 Micronaire reading, and it was noted at this time that the bobbins using the 5.1 cotton still had approximately $\frac{1}{4}$-in. clearance from the ring, and their travelers were not yet rubbing (Figure 11). (These bobbins were

moved to the same side of the frame to simplify photographing.) The bobbins on the left almost fill the rings, whereas those on the right do not. This is even more evident from the soiling of the yarn by the traveler, as seen in Figure 12. The builder motion had previously been set to accommodate the fine cotton. Measurement of the bobbin diameters showed there was approximately $\frac{1}{4}$ in. difference in the bobbin diameters, those spun from the fine cotton being larger.

Since it was possible that the tension under which the yarns were wound onto the spinning bobbins was different, which could cause a difference in bobbin diameter, fourteen 120-yard skeins from each set of yarn were wound onto paper tubes. In order to ensure the packages being wound under the same tension, they were then rewound onto other tubes, the diameters of which had been checked carefully. The diameters of the packages were then measured, and it was found that the yarn spun from the fine cotton produced a package $\frac{1}{16}$ in. larger in diameter than the package produced from an equal yardage of yarn spun from the coarse cotton. This entire procedure was repeated twice, beginning at the roving frame and using different sets of spinning spindles each time. Again, using 1680-yd. packages wound on tubes, the results were essentially the same. Listed below are the mean yarn numbers (based on the fourteen measured skeins from each test) and the actual twist of these yarns:

| | Yarn number | Twist (T.P.I.) |
|---|---|---|
| Coarse cotton (5.1) | 13.3 | 16.2 |
| Fine cotton (3.0) | 13.2 | 16.2 |

These findings were a further indication that the fibers possessing the lower Micronaire readings produce yarns with larger effective diameters. It was not, however, a direct measurement of yarn diameter.

Samples of the roving from the $\frac{29}{32}$-in. cottons with Micronaire readings of 3.1 and 6.2 were then used to spin 22's yarns, the necessary adjustments being made until the following results were obtained:

| | Yarn number | Twist (T.P.I.) |
|---|---|---|
| Coarse cotton (6.2) | 22.0 | 21.5 |
| Fine cotton (3.1) | 22.0 | 21.6 |

Twenty specimens from each of these yarns were taken over a length of 120 yd. at approximately 5-yd. intervals. These specimens were impregnated, at the same time and while being held under equal tension, with a solution of acetone and collodion by alternating the pressure in a vacuum chamber. Upon drying, and in the rigid state thus produced, three cross sections were cut from each specimen, making a total of 60 cross sections from each of the two yarns. Using a microscope equipped with a micrometer, the area of each yarn cross section was approximated. Since very few of the sections indicated a cylindrical yarn, a major axis and minor axis, one being at a 90° angle to the other, were measured on each section. Actually, the sections exhibited many different geometric figures: circle, square, hexagon, ellipse, etc. Also, due to the boundaries of the sections being somewhat indefinite, each section was measured by two operators. The mean results obtained from the 120 observations on each yarn were as follows:

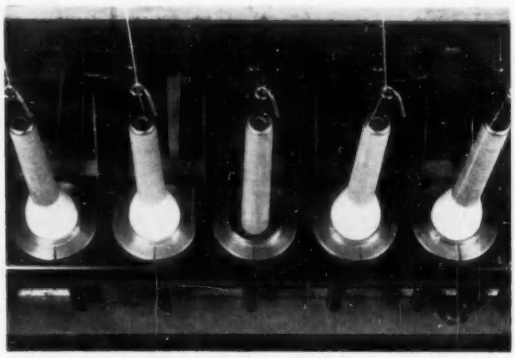


**Fig. 11.** Photograph (top view) showing bobbins of yarn spun from cottons with 3.0 Micronaire reading (left), 5.1 Micronaire reading (right).

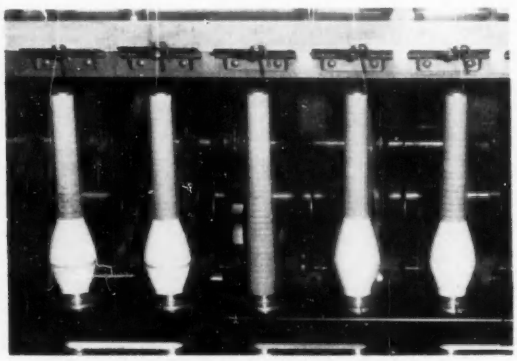
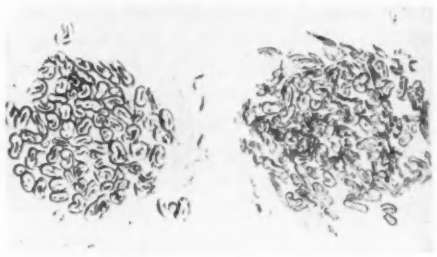


**Fig. 12.** Photograph (side view) showing bobbins of yarn spun from cottons with 3.0 Micronaire reading (left), 5.1 Micronaire reading (right).

| | Yarn diameter | | Cross-sectional area |
|---|---|---|---|
| | Axis *x* (microns $\times 10^2$) | Axis *y* (microns $\times 10^2$) | (microns$^2$ $\times 10^2$) |
| Fine cotton (3.1) | 5.21 | 5.40 | 22.08 |
| Coarse cotton (6.2) | 4.87 | 5.14 | 19.64 |

The mean axes of the yarns from the 3.1 cotton showed an increase of 6.0% as compared with the yarns from the 6.2 cotton and an increase of 12.4% in cross-sectional area. The sections shown in Figure 13 were selected for illustrative purposes because they approximate the average result. It was also noted that the cross sections of the yarns spun from the fine cotton showed the largest number of uncontrolled fibers near the outer boundaries. This characteristic, which possibly adds to the effective diameter, was observed throughout the series of cross sections.



a b

**Fig. 13.** Photomicrograph of cross sections of 22's yarns spun from cottons with *a*, 6.2 Micronaire reading, *b*, 3.1 Micronaire reading.

## Summary and Conclusions

A coefficient of multiple linear correlation of 0.830 was found for the relationship existing between the amount of weaving contraction in the coarse sheeting fabric and the three collective variables considered. These variables—fiber fineness (Micronaire), staple length, and filling twist—accounted for approximately two-thirds of the variance in the amount of weaving contraction. The multiple correlation coefficient for the combination of fineness and staple length was 0.817. Fineness alone explained almost as much of the variance, the partial correlation coefficient being 0.805. The partial correlation coefficient for staple length was 0.660 and only 0.235 for twist.

The influence of these three factors on the amount of weaving contraction in the fabric rank in descending order of importance as follows:

1. Fiber fineness (Micronaire)
2. Staple length
3. Twist (T.P.I.)

The correlation analyses indicate an inverse relationship between Micronaire readings and weaving contraction; i.e., within the range of fineness studied, the amount of weaving contraction increased as the Micronaire readings decreased. These analyses also indicated a direct relationship between staple length and weaving contraction, the latter increasing with an increase in staple length. The weaving contraction increased slightly, but not significantly, with an increase in T.P.I. within the range of twist studied. It is possible that a part of the increase in the percentage of weaving contraction, concomitant with the use of yarns spun from cottons with lower Micronaire readings, was the result of an increase in effective twist. Since the yarns spun from the fine cottons were found to be larger in diameter than those spun from the coarser cottons, yet were spun with the same number of turns per inch, they actually possessed a higher effective twist.

The results of this study indicate that fiber fineness, as measured by the Micronaire, has a significant influence on the amount of weaving contraction. This change in the amount of weaving contraction is caused, at least in part, by differences in yarn diameters, which are in turn a function of fiber fineness. As the coarser cottons are used, the diameter of the yarn becomes smaller (when comparing the same counts), thereby causing less weaving contraction.

Since methods are not readily available for determining the influence of certain other factors which may affect weaving contraction, such as yarn flexibility, the degree of flattening, and inherent yarn contraction, it cannot be ascertained whether or not all of the change in contraction attributed to fiber fineness was the result of variations in yarn diameter. Whether or not this same relationship will be found in constructions other than plain weaves is beyond the scope of this study; however, it does seem reasonable to assume than a significant difference will be observed in most plain woven fabrics.

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